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Spectral Measurements of Gaseous Sulfuric Acid Using Tunable Diode Lasers

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ABSTRACT

Using a tunable diode laser spectrometer with a spectral resolution of about 10^{-4} cm^{-1}, the important central portions of the two infrared absorption bands of H_2SO_4 at 8.2 μm (1222 cm^{-1}) and 11.3 μm (880 cm^{-1}) have been scanned at low pressure (~0.67 Torr of H_2SO_4) and at atmospheric nitrogen pressure. Maximum absorption coefficients have been measured to be 6.5 cm^{-1}/atm and 6.9 cm^{-1}/atm at the 8.2 μm (1222 cm^{-1}) and 11.3 μm (880 cm^{-1}) bands respectively. Interference spectra of SO_2, CO_2 and H_2O near the H_2SO_4 absorption peaks at 1222 cm^{-1} and 880 cm^{-1} were scanned using a 1.1 m cell at 200°C to determine interference-free regions. A spectroscopic method was used to measure the partial pressures of H_2SO_4, SO_3 and H_2O vapors above azeotropes of H_2SO_4 at 107°C, 150°C and 200°C. The expected performance characteristics of an H_2SO_4 tunable diode laser stack monitor are considered on the basis of the above results.

CONTENTS

Abstract..... iii
Figures..... vi
Tables..... viii

1. Introduction..... 1
2. Summary..... 4
3. Conclusions..... 6
4. Recommendations..... 8
5. Experimental Apparatus, Methods and Results..... 11
   - High resolution absorption measurements of low pressure H_2SO_4 vapor..... 10
   - High resolution absorption measurements of H_2SO_4 vapor in atmospheric pressure of nitrogen..... 23
   - High resolution absorption measurements of interferants - H_2O, SO_2 and CO_2..... 32
   - Spectroscopic determination of partial vapor pressures above hot azeotropic H_2SO_4 solution..... 42

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FIGURES

Number		Page
1	Low-pressure H_2SO_4 absorption measurement setup.....	12
2	Low-pressure H_2SO_4 absorption cell.....	14
3	Absorption spectra above hot H_2SO_4 solution (T~165°C).....	16
4	H_2SO_4 absorption near 1223 cm^{-1}.....	17
5	Low-pressure absorption H_2SO_4 absorption near 1224 cm^{-1}.....	19
6	Low-pressure H_2SO_4 absorption near 880.5 cm^{-1}.....	20
7	Strip chart recording of low pressure H_2SO_4 absorption vs. time.....	21
8	Low pressure H_2SO_4 absorption (P~0.67 Torr T=170°C).....	22
9	Low pressure H_2SO_4 absorption (P~0.67 Torr T=170°C).....	24
10	Experimental setup for H_2SO_4 absorption at atmospheric N_2 pressure.....	25
11	Absorption cell for H_2SO_4 absorption at atmospheric nitrogen pressure and H_2SO_4 vapor generator.....	26
12	H_2SO_4 absorption at atmospheric nitrogen pressure....	28
13	H_2SO_4 absorption at atmospheric nitrogen pressure....	29
14	H_2SO_4 absorption at atmospheric nitrogen pressure....	30
15	H_2SO_4 absorption at atmospheric nitrogen pressure....	31
16	Location of the 2 cm^{-1} atmospheric scan region with respect to the 1210-1240 cm^{-1} low-pressure scan....	33

Number		Page
17	H_2SO_4 absorption at atmospheric nitrogen pressure....	34
18	H_2SO_4 absorption at atmospheric nitrogen pressure....	35
19	H_2SO_4 absorption at atmospheric nitrogen pressure....	36
20	H_2SO_4 absorption at atmospheric nitrogen pressure....	37
21	H_2SO_4 absorption at atmospheric nitrogen pressure....	38
22	Location of the 2 cm^{-1} atmospheric scan region with respect to the 870-895 cm^{-1} low pressure scan.....	39
23	SO_2 absorption near 1222 cm^{-1}.....	40
24	SO_2 absorption.....	41
25	H_2O absorption.....	43
26	H_2O absorption.....	44
27	CO_2 absorption.....	45
28	H_2O absorption.....	46
29	Absorbance per unit pressure (αL/Torr) vs. temperature of cell body for the H_2O line at 1330 cm^{-1} (L=64 cm).....	48
30	H_2O line at 1330 cm^{-1} above a 150°C H_2SO_4 azeotrope L=64 cm, T_{body}=170°C.....	49
31	Absorbance per unit pressure (αL/Torr) vs. temperature of cell body for the SO_3 line near 1354 cm^{-1} (L=64 cm).....	50
32	SO_3 absorption lines near 1354 cm^{-1}.....	51
33	Total pressure measurement apparatus.....	54
34	Dissociation constant K_p of H_2SO_4 gas vs. temperature.....	58
35	Partial pressure of H_2SO_4, H_2O and SO_3 above azeotropic H_2SO_4 solution vs. temperature.....	59
36	Total vapor pressure above H_2SO_4 solution vs. azeotropic composition.....	62

TABLES

Number		Page
1	H_2O Partial Pressure vs. Temperature of H_2SO_4 Azeotrope	52
2	SO_3 Partial Pressure vs. Temperature of H_2SO_4 Azeotrope	52
3	Total Pressure vs. Temperature of H_2SO_4 Azeotrope	55
4	H_2SO_4 Partial vs. Temperature of H_2SO_4 Azeotrope	55
5	Azeotropic Composition vs. Temperature of H_2SO_4 Azeotrope	57
6	Calculated Partial Pressures Including the Effects of Dissociation	61

SECTION 1

INTRODUCTION

The central purpose of this program was to determine the high resolution spectral properties of H_2SO_4 and of possible interferants H_2O, SO_2, SO_3 and CO_2. This information is needed to evaluate the potential sensitivity of and design a sensitive stack gas monitor based on tunable laser techniques.

There is considerable environmental interest in sulfuric acid because of its damaging effect on the ecologic system and strongly suspected adverse health effects on humans (1). The presence of sulfuric acid in air is mainly due to the burning of sulfur-bearing fuels, particularly coal, which is projected to become a widely-used, major fuel in the coming years. While the primary combustion product is fulfur dioxide, 1 to 10% may be emitted as trioxide, which reacts rapidly with moisture in the atmosphere to produce H_2SO_4. Furthermore, SO_2 may be oxidized to form H_2SO_4, and this is an efficient process in the presence of catalysts such as platinum, vanadium pentoxide and oxides of nitrogen (most commercial methods of producing H_2SO_4 rely on the catalytic oxidation of SO_2).

Monitoring H_2SO_4 by spectroscopic techniques require that the relevant parameters of H_2SO_4 be known. A number of investigators (2-4) have published low-resolution, qualitative band spectra of H_2SO_4 vapor in the infrared spectral region.

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1. West, P. W., A. D. Shendrikar and N. Herrara. Analytica Chimica Acta 69, 111 (1974).

2. Stopperka, K. "The Infrared Spectrum of the Water-free H_2SO_4 and the Composition of the H_2O-H_2SO_4 System." Zeit fur Anorgan und Alleg. Chem. 344, 263-278 (1963).

3. Chackalackal, S. M. and F. E. Stafford. "Infrared Spectra of the Vapors above Sulfuric and Deuteriosulfuric Acids." Journ. Amer. Chem. Soc., 88:4, 723-728, Feb. 20, 1966.

4. Stopperka, K. and F. Kilz. "Die Zusammersetzung der Gasphase über dem flüssigen System H_2O-H_2SO_4 in Abhängigkeit von der Temperatur." Z. anorg. u allgem. Chem., Band 370, 49-66, 1969.

According to these published works, there are four infrared bands of H_2SO_4 centering at 2.8 μm, 6.9 μm, 8.2 μm and 11.3 μm. Because of very strong interference by H_2O for the first two bands, only the last two bands are worth considering for monitoring purposes.

Besides the low resolution absorption data mentioned above, high resolution spectra of H_2SO_4 vapor from 1312 to 1549 cm^{-1} have been published by Alpert (5). Since they lie in the 6.5 μm band of H_2O, they are of little use for monitoring purposes. However, the author did identify many individual lines as being H_2SO_4. On this basis, it might be expected that there are similar individual H_2SO_4 absorption lines in the 8.2 μm and 11.3 μm bands which would be suitable for monitoring purposes.

Most recently, quantitative low resolution (~1 cm^{-1}) spectra of the 1220 and 880 cm^{-1} bands of H_2SO_4 have been obtained independently by Burch and co-workers (6) at Aeronutronic Ford and R. Majkowski (7) at the General Motors Research Laboratory. The maximum absorption strength observed with low resolution in these bands is approximately 2 to 5 cm^{-1} atm^{-1} (.0002 to 0.0005 m^{-1}/ppm). While these absorption strengths appear to be adequate for infrared monitoring H_2SO_4 in stack gas, the lack of spectral structure (e.g., isolated lines) at low resolution seriously complicates the monitoring task. Strong interferences further complicate the monitoring since there are few, if any, 1 cm^{-1} spectral intervals in the H_2SO_4 bands free of absorption due to H_2O, CO_2 and SO_2. High resolution (<0.01 cm^{-1}) spectra are required to identify the strongest H_2SO_4 absorption lines and reveal any absorption features which would be useful in the design of a monitoring instrument. High resolution spectra of CO_2, SO_2 and H_2O at elevated temperatures are also needed to determine the severity of the interference problem for a low resolution (1-5 cm^{-1}) monitoring instrument and to locate spectral windows free of interference for a laser monitoring instrument.

The primary difficulty in carrying out high resolution spectroscopy of hot H_2SO_4 is in the area of gas cell design and gas handling. Reading of the above mentioned EPA report (6) and the

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5. Alpert, B. D. "Studies in High Resolution Infrared Spectroscopy." Ph.D. Dissertation. (Appendix B contains H_2SO_4 data.) Ohio State University, Columbus, Ohio, 1970.

6. Burch, D. E., F. J. Gates and N. Potter. "Infrared Absorption by Sulfuric Acid Vapor." FINAL REPORT NO. EPA-600/2-76-191, July 1976.

7. Majkowski, R. F. "Infrared Absorption Coefficient of H_2SO_4 Vapor from 1190 to 1260 cm^{-1}." J. Opt. Soc. Am. 67, 624, 1977.

recently published journal article (7) indicate that there have been many problems encountered in fabricating and using suitable infrared gas cells. Neither Aeronutronic Ford nor General Motors has obtained high resolution spectra of the pure azeotropic H_2SO_4 at a known (measured) temperature and pressure. All of General Motors' spectra were obtained in a flowing system at atmospheric pressure using N_2 as a carrier gas. The temperature of the H_2SO_4 vapor studied by Aeronutronic could only be inferred from pressure measurements. This report describes an approach to cell design to obtain the desired spectral absorption data at the highest resolution available with tunable diode lasers.

In this report, the experiments and the results of high resolution scans of H_2SO_4 vapor at low pressure and at atmospheric nitrogen pressure will be presented for the spectral regions centering at 8.2 μm and 11.3 μm. In addition, high resolution scans of H_2O, CO_2 and SO_2 gases conducted to determine the lowest interference regions for H_2SO_4 vapor monitoring will be discussed.

In order to monitor the concentration of H_2SO_4 vapor in a smoke stack gas, which has a temperature range from about 150°C to 250°C, it is necessary to determine the absorption coefficients of H_2SO_4 vapor at this temperature range. Because of the dissociation of H_2SO_4 into H_2O and SO_3 (8), partial pressures are known only for solutions with rather low H_2SO_4 concentration and for the atmospheric azeotrope (9). The solutions with low H_2SO_4 concentration are not azeotropes and are therefore difficult to be reproduced reliably in the laboratory for absorption measurements. The partial pressures at different temperatures of an atmospheric H_2SO_4 azeotrope have been measured (9). However, since the vapor phase and liquid phase are not in equilibrium at any temperature other than 326°C, the partial pressures will depend on the temperature and volume of the vessel or container. Based on the above reasoning, it is best to work with azeotropes in the stack temperature range of 150 to 250°C for reliable reproducibility.

Tunable diode lasers offer a convenient method of measuring the partial pressure of H_2O and SO_3 vapors directly. The partial pressure of H_2SO_4 vapor can then be determined by subtracting the SO_3 and H_2O partial pressures from the total vapor pressure. In this report, a spectroscopic method and results of partial pressure determination will be presented.

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8. Gmitro, J. I. and Vermeulen. "Vapor-Liquid Equilibria for Aqueous Sulfuric Acid." A. I. Ch. E. Journal 10, 740 (1964).

9. Luchinskii, G. P., Zhur. Fl2 Khim, 30, 1207 (1956).

SECTION 2

SUMMARY

Using the highest spectral resolution (~10^{-4} cm^{-1}) presently available with tunable diode lasers, important central portion of the H_2SO_4 bands at 8.2 μm (1222 cm^{-1}) and 11.3 μm (880 cm^{-1}) have been scanned at low pressure (~0.67 Torr of H_2SO_4) and at atmospheric pressure with nitrogen as the main gas. Because of the extremely corrosive nature of hot H_2SO_4 and SO_3, cell design and construction were carefully carried out. The result was that there were no visual or spectrally-detectable contamination in the cell after many hours of cell operation near 200°C. Due to the complex thermodynamic nature of the vapors above a hot H_2SO_4 solution, only azeotropes of H_2SO_4 solution prepared from standard solution by a distillation method were used throughout in the experiments.

In a low pressure scan of a sealed-off H_2SO_4 cell from 1210-1240 cm^{-1}, two peaks were observed. They are located near 1222 cm^{-1} and 1235 cm^{-1}, the former being sharper and stronger than the latter. Similar low-pressure scan in the range 870-895 cm^{-1} shows only one peak at 880 cm^{-1}. The absorption coefficients are found to be 7.2 and 7.0 cm^{-1}/atm at 1222 cm^{-1} and 880 cm^{-1} respectively. Besides these rather broad (>2 cm^{-1}) spectral peaks, there were no sharp individual H_2SO_4 lines throughout nearly the whole of the two spectral regions.

Using a flowing-gas cell with dry nitrogen as the carrier gas, atmospheric scans were performed at liquid H_2SO_4 reservoir temperatures of 180°C and 200°C over 2 cm^{-1} intervals near 1222 cm^{-1} and 880 cm^{-1}. Absorption coefficients of 6.5 cm^{-1}/atm (6.5 x 10^{-4} ppm^{-1}-m^{-1}) and 6.9 cm^{-1}/atm (6.9 x 10^{-4} ppm^{-1}-m^{-1}) have been obtained at 1222 cm^{-1} and 880 cm^{-1} respectively.

Using a 1.1 m cell operated at 200°C, interference spectra due to SO_2, H_2O and CO_2 were scanned over the same two cm^{-1} intervals. In the 1222 cm^{-1} peak region, the SO_2 spectra exhibit a very high line density. The H_2O absorption is much stronger at 1222 cm^{-1} than at 880 cm^{-1}. In the 880 cm^{-1} region, CO_2 absorption at 100 Torr pressure was not detectable at a cell length of 1.1 m.

Spectra of H_2O and SO_3 and SO_2 were all easily observed with a 50 cm low pressure cell, when the liquid H_2SO_4 reservoir was heated to about 100°C or higher.

The partial pressures of SO_3 and H_2O above H_2SO_4 azeotropes at several temperatures (107°C, 150°C and 200°C) were determined spectroscopically. This was done by measuring the absorption strengths of H_2O and SO_3 lines and comparing them against calibrated absorption strengths, the calibrated strengths being determined using either H_2O or SO_3 alone in the absorption cell. A "U" tube manometer in which the fluid in the "U" tube was an H_2SO_4 azeotrope was used to measure the total vapor pressure. The partial pressure of H_2SO_4 vapor was then given by the difference between the total pressure and the sum of the SO_3 and H_2O partial pressures. The H_2SO_4 partial pressures above azeotropes at different temperatures obtained in the present experiment are about 30 percent smaller than those reported by Luchinskii (9) for the atmospheric azeotrope at the corresponding temperatures. The present results were used to compute the absorption coefficient of H_2SO_4 vapor at different temperatures.

SECTION 3

CONCLUSIONS

At low pressure, the H_2SO_4 vapor spectrum has a dense, fine structure near the 8.2 μm band center, ~1223 cm^{-1}. The width of this fine structural band is only about 0.5 cm^{-1}. Since the observed line spacing is about 0.01 cm^{-1}, it was expected and experimentally confirmed that this fine structure would be smoothed out at atmospheric pressure. For stack monitoring of H_2SO_4 vapor, it is necessary to use the broad smooth peak (>2 cm^{-1}) observed at atmospheric pressure. The maximum percentage change in absorption strengths occurs on the side of a peak at 1222 cm^{-1}. It has a slope of about 35%/cm^{-1} at atmospheric pressure, whereas the absorption signal at the peak is about 1% for a 15 ppm-m H_2SO_4 concentration. The detection of this level of absorption change can be met using state-of-the-art tunable diode laser techniques. The partial pressure of H_2SO_4 obtained in the present experiment is about 30 percent smaller than those reported by Luchinskii (9). As a result, the detection limit for H_2SO_4 vapor is correspondingly lower, ~2 ppm-m. The intensity of individual SO_3 lines have been measured, for the first time, as a function of temperature for the ν_3 band centering at 1391 cm^{-1}. It appears that the present technique of partial pressure measurements can be extended to include study on the thermodynamics of $2SO_3 \rightleftarrows 2SO_2 + O_2$. This last catalytic reaction has been known to exist both in stack gas and in automobile exhaust.

Based on the present experimental result, a monitoring instrument utilizing the 880 cm^{-1} absorption peak should be a dual wavelength absorption type. One wavelength would be fixed near 880 cm^{-1}, where there is strong H_2SO_4 absorption coupled with low interference from H_2O and CO_2. The other wavelength would be at a region about 1000 cm^{-1}, where there is very little absorption by H_2SO_4, SO_2, CO_2 or H_2O. Subtracting the absorptions measured at these two wavelengths will produce a signal proportional to the H_2SO_4 concentration. The two wavelength technique has been used in long-path monitoring of atmospheric pollutants (10). Comparison with this earlier work indicates that 4 ppm-m of H_2SO_4 can be measured, neglecting the difference in

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10. Menzies, R. T. and M. S. Shumate. "Remote Measurements of Ambient Air Pollutants with a Bistatic Laser System." Appl. Opt. 15, 2080, 1976.

pathlength and environment. This compares with an estimated interference-limited sensitivity of about 2 ppm-m. Only the known interferants, H_2O and CO_2, have been considered.

The principal advantage of using a tunable, narrow-line source is the ability to select frequencies that lie in clear spaces within the densely spaced interference lines of H_2O and hot CO_2. With a conventional infrared source, such as a Nernst glower filtered by a grating spectrometer, energy consideration dictates a spectral slitwidth of about 1-2 cm^{-1}, which is wider than interference line spacings. Thus, a field instrument using conventional spectrometer will fail to maintain accurate calibration due to fluctuations in temperature and concentrations of CO_2 and H_2O.

SECTION 4

RECOMMENDATIONS

Based on the experimental results on atmospheric H_2SO_4 absorption measurements and on SO_2, H_2O and CO_2 interference measurements, the ultimate sensitivity of a monitoring instrument is likely to be limited by interference. This is especially true for the 1222 cm^{-1} region where the SO_2 lines are very dense. Therefore, it is recommended that a laser spectrometer be used for H_2SO_4 vapor detection. The main advantage of this type of instrument is that it is least subject to interference, since the wavelength of operation can be tuned to a region away from absorption lines.

A dual wavelength absorption method using two diode lasers appears to be the best approach at the present. One laser should be tuned to the absorption peak near 880 cm^{-1} and the other near 1000 cm^{-1}, where H_2SO_4 absorption is low. An absorption calibration can be made by inserting a short cell containing H_2SO_4 vapor in atmospheric nitrogen into the beam path. The cell design should use a permanent, stable, sealed-off feature similar to that in the present study. For the highest stability in laser frequency, the lasers would be frequency locked to absorption line center. The system should use a retroreflector to increase the pathlength. High frequency modulation techniques (>10 kHz) should be employed to minimize turbulence effects. The results of this study indicate that the existence of interferences will severely limit the performance of a conventional IR instrument for monitoring H_2SO_4 in stacks, but that sufficient sensitivity can be achieved with a tunable diode laser instrument.

It has been shown that the partial vapor pressures of H_2O, SO_3 and H_2SO_4 can be determined spectroscopically. The degree of dissociation indicated by the equation $H_2SO_4 \rightarrow H_2O + SO_3$ can also be measured spectroscopically by monitoring the SO_3 and H_2O absorptions for different cell wall temperatures at a given H_2SO_4 reservoir temperature.

The SO_3 molecule is also of interest. The present high resolution laser spectrometer should be useful in measuring all the SO_3 lines in the ν_3 band. Such spectroscopic parameters as line strength and pressure broadening can easily be determined. The result could be helpful in further understanding catalytic reactions such as $2SO_2 + O_2 \rightleftharpoons 2SO_3$.

It appears that the fine absorption structure near 1223 cm^{-1} might be that of gaseous H_2SO_4. It would seem worthwhile to further pursue similar high resolution measurements at this and other regions using a longer cell. Increasing the cell path-length to 10 meters would permit an operating temperature reduction to 80°C or below. At this lower temperature, pressure broadening is probably negligible and fewer hot vibrational bands are present.

In future experiments with H_2SO_4 vapor, the source of SO_2 in a low-pressure cell, as detected in the present experiment, should be determined. If it is an impurity in H_2SO_4 it should be purged with helium bubbling through the hot H_2SO_4 liquid. Since the presence of SO_2 can be monitored spectroscopically, the effect of purging can be observed.

Finally, the "U" tube manometer used for the total pressure measurement has been proven to be a rather simple instrument to use. It is recommended that it be used in a system where only moderately precise pressure measurements are required. An all quartz spiral gauge should be employed for more precise pressure measurements.

SECTION 5

EXPERIMENTAL APPARATUS, METHODS AND RESULTS

In this section of the report, we shall first outline the specific tasks required. For each task, we will discuss the apparatus and methods used and the experimental results. The following is a list of required tasks:

- High Resolution Absorption Measurements of Low Pressure H_2SO_4 Vapor. Spectral measurement is to be performed with a suitable spectrometer system at the azeotropic point of the H_2SO_4-H_2O vapor liquid phase diagram. Spectral scans throughout the 870-895 cm^{-1} and 1210-1240 cm^{-1} regions are required.

- High Resolution Absorption Measurements of H_2SO_4 Vapor in Atmospheric Pressure of Nitrogen. Upon identification of prominent H_2SO_4 absorption lines in both spectral regions, atmospheric H_2SO_4 absorption measurements are to be performed with continuous coverage of at least 2 cm^{-1} and centered on the most prominent peak in each region.

- High resolution Absorption Measurements of Interferants - H_2O, SO_2 and CO_2. Absorption spectra of H_2O, CO_2 and SO_2 shall be obtained in the identical spectral regions and under similar experimental conditions.

- Spectroscopic Determination of Partial Vapor Pressures above Hot Azeotropic H_2SO_4 Solution. The partial pressures of H_2O, SO_3 and H_2SO_4 vapors are to be determined spectroscopically for azeotropes of H_2SO_4 at 100, 150, 200 and 250°C.

The above measurements shall be performed with a resolution equal to or better than 0.05 cm^{-1} and all spectral line positions shall be referenced with respect to known spectral lines.

HIGH RESOLUTION ABSORPTION MEASUREMENTS OF LOW PRESSURE H_2SO_4 VAPOR

Experimental Apparatus and Methods

Figure 1 is a schematic diagram of the experimental setup which was employed to perform the low-pressure H_2SO_4 absorption measurements from 1210-1240 cm^{-1} and from 890-895 cm^{-1}.

A diode laser of either $Pb_{0.989}Sn_{0.011}Se$ (1220 cm^{-1} band) or $Pb_{0.955}Sn_{0.045}Se$ (880 cm^{-1} band) was mounted on a vibrationally-isolated cold finger of a closed-cycle cryogenic cooler. The required fractional value of tin depends on the composition-to-wavelength tuning characteristics of the material. The temperature of the cold finger was accurately controlled to ±0.0003°K anywhere in the range from 12°K to 80°K by the temperature controller. In operation, the laser frequency was tuned grossly by changing the cold finger temperature and finely by changing the laser diode injection current, supplied by the diode current power supply. The cryogenic cooler, the temperature controller and the diode current power supply are major components of a laser spectrometer system (Laser Analytics, Inc. Model LS-3). As shown in the diagram, the laser radiation is collected by a 2.5 cm f.l., f/1 lens and is steered into a 25 cm long pyrex absorption cell. The far end of the pyrex cell was gold coated for efficient spectral reflection. After traversing the cell twice, the beam is directed into a grating monochromator for spectral mode filtering. The transmitted beam is then detected, synchronously amplified and is displayed on an x-y recorder. The drive for the x-axis of the x-y recorder is proportional to the diode current. For absolute frequency calibration a reference gas cell was used. For relative frequency calibration, a fixed Ge etalon with a free spectral range of 0.04844 cm^{-1} at 1222 cm^{-1} (0.04856 cm^{-1} at 880 cm^{-1}) was used.

The procedure used in absorption measurement is as follows:

1) perform a background scan with no H_2SO_4 vapor present in the cell, H_2SO_4 reservoir at 60°C or lower

2) perform a reference frequency scan with a reference gas cell in the beam path

3) perform an etalon scan

4) perform an H_2SO_4 absorption scan with hot H_2SO_4 vapor in the cell, H_2SO_4 reservoir at 100°C or higher.

The cell wall temperature is to be maintained at a higher (10 to 15°C) temperature than that of the reservoir for all of the above steps.

The design and construction of the H_2SO_4 absorption cell is of the utmost importance in the success of the experiment, since hot H_2SO_4 acid is corrosive to many vacuum and optical material coming in contact with it.

For the low-pressure H_2SO_4 cell, pyrex glass tubing was used for the cell body. The inside diameter of the tubing was 28 mm. One end of the cell has a gold-coated flat pyrex mirror.

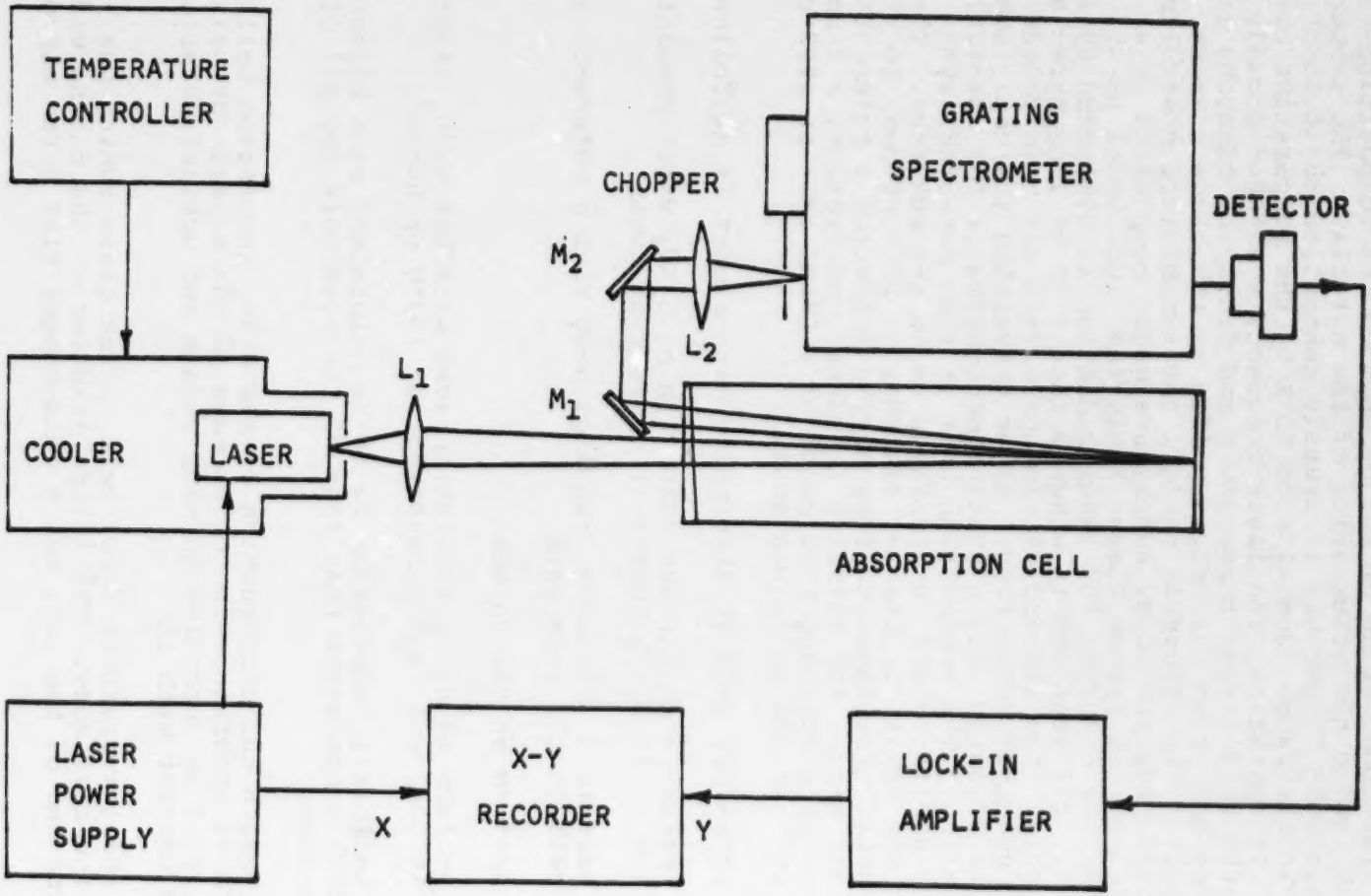

Figure 1. Low-pressure H_2SO_4 absorption measurement setup

The other end has a 1 mm thick, optical-grade silicon window with a 2° widge. The cell length from the window to the gold mirror is 25 cm. A tight vacuum seal was successfully made between the Si window and the pyrex glass tube (pyrex No. 332) by shrinking the I.D. of the latter on the edge of the silicon window at high temperature (~800°C). The seal could apparently withstand repeated cycling between 20°C and 275°C without deterioration as witnessed at the end of the low-pressure absorption measurements that the absorption linewidth of SO_2 (in minute presence in the cell possibly as an impurity in H_2SO_4) remained quite narrow. This is a condition indicating a low background pressure in the cell.

To conveniently control the vapor pressure of H_2SO_4 in the low-pressure cell, a pyrex side arm was incorporated into the cell. Figure 2 is a picture of the low-pressure cell with liquid H_2SO_4 in the side arm. In operation, the cell body was typically at about 200°C while the side arm was at a lower temperature. The side arm temperature was controlled independently by surrounding the side arm with a heatable copper tube. A thermocouple attached to the tip of the side arm tube sensed the liquid H_2SO_4 temperature and was part of a feedback temperature control system. In a background scan, the heater to the copper tube was turned off and the side arm temperature was cooled down to below 60°C. For an absorption scan, the heater was automatically turned off and on to maintain a preset temperature (~170° ± 1°C) on the liquid H_2SO_4.

The cell was baked out at 250°C and back filled with dry nitrogen. Then a few cm^3 of a 37N H_2SO_4 solution (98.5 to 99.3% H_2SO_4 concentration) was placed on the side arm reservoir. The azeotrope was prepared by evacuating about a third of the original H_2SO_4 acid in the reservoir at 160°C. Here we followed conservatively the recommendation by Kunzler (11) who obtained an atmospheric azeotrope by boiling off 20 percent of an original 91.9 wt.% H_2SO_4 solution. Since the H_2SO_4 partial pressure near the azeotropic composition is insensitive to a change in the azeotropic composition (8), a small change, if any, in the azeotropic composition does not affect the H_2SO_4 absorption coefficient measurement result. The low pressure cell was permanently sealed off for absorption measurements.

Experimental Results

Since the vapors above azeotropic solution of H_2SO_4 are H_2O, SO_3 and H_2SO_4, it is desirable to identify their presence. Scanning the low-pressure cell at high resolution is one way of searching for them. For strong H_2O lines, the positions are

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11. Kunzler, J. E. Anal. Chem. 25, 93 (1953).

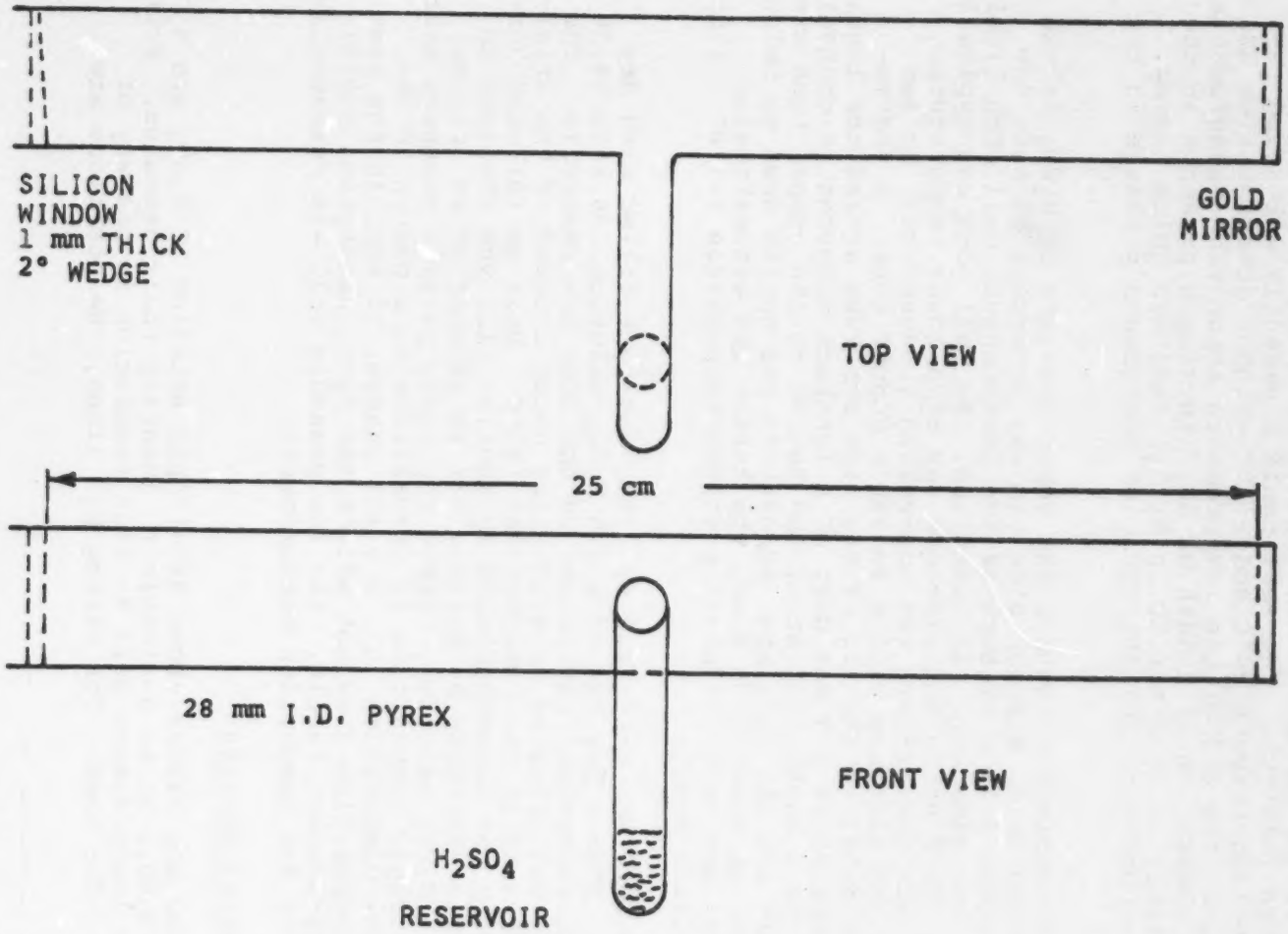

Figure 2. Low-pressure H_2SO_4 absorption cell

known to better than 0.05 cm^{-1}. For SO_3, from the work of Lovejoy (12), it is known that there is a strong absorption band centered at 1391 cm^{-1}. Using the experimental setup shown in Fig. 1 and a diode laser tuned to the 1400 cm^{-1} region, a spectrum of SO_3 lines and one H_2O line was obtained. Figure 3 shows a scan near the 1416.13 cm^{-1} H_2O line. These data were taken with the H_2SO_4 reservoir near 165°C and the cell wall temperature about 180°C. Since an atmospheric path of about 2.2 m was in series with the cell, absorption by atmospheric H_2O vapor shows up as a broad dip. The H_2O vapor in the low-pressure cell shows up as a narrow line located at the center of the atmospheric water line. The rest of the lines are all SO_3. The SO_2 band centered about 1375 cm^{-1} does not extend far in this region even at high temperature. A 30 cm cell filled with 10 Torr of SO_2 at 200°C shows no absorption lines when scanned in this region. Further evidence that the observed lines in Fig. 3 are SO_3 is that the width of the H_2O line (in an expanded scale) is greater than that of the SO_3 lines. At low pressure, the widths are due to Doppler broadening. The measured linewidths are 0.0055 cm^{-1} for the H_2O line and 0.0028 cm^{-1} for SO_3 lines. The calculated linewidths are 0.005 cm^{-1} and 0.0024 cm^{-1}. The measured width of SO_3 appears slightly too great in comparison with the calculated value. This is perhaps due to pressure broadening. These are spectroscopic evidences that the vapors above hot H_2SO_4 solution did contain H_2O and SO_3 and they are detectable by tunable diode laser spectroscopy.

After H_2O and SO_3 absorption lines were observed, the laser was tuned to the 8.2 μm region in searching for H_2SO_4 absorption lines. Figure 4 is a recorder trace of H_2SO_4 vapor absorption near 1223 cm^{-1}. The cell body was operated at about 200°C while the liquid H_2SO_4 reservoir was at 170°C and 155°C for the two absorption scans. The reference lines are N_2O lines. The calibration trace was obtained with a 16 cm cell filled with 10 Torr of N_2O gas. The frequency of one of the N_2O line was identified to be 1223.36 cm^{-1} (13).

The dotted trace near the bottom is the etalon scan with a fringe spacing 0.0484 cm^{-1}. By counting the number of fringes, the width of this scan was calculated to be about 0.6 cm^{-1}. This width is typical for diode lasers in this spectral region. As can be seen, the absorption traces show that there are fine

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12. Lovejoy, R. W., J. H. Colwell, D. R. Eggers and G. D. Halsey. "Infrared Spectrum of Gaseous Sulfur Trioxide." J. Chem. Phys., 36, 612 (1962).

13. McClatchey, R. A., W. S. Benedict, S. A. Clough, D. E. Burch, R. F. Calfee, K. Fox, L. S. Rothman and J. S. Garing. "AFCRL Atmospheric Absorption Line parameters Compilation." AFCRL-TR-73-0096, 1973.

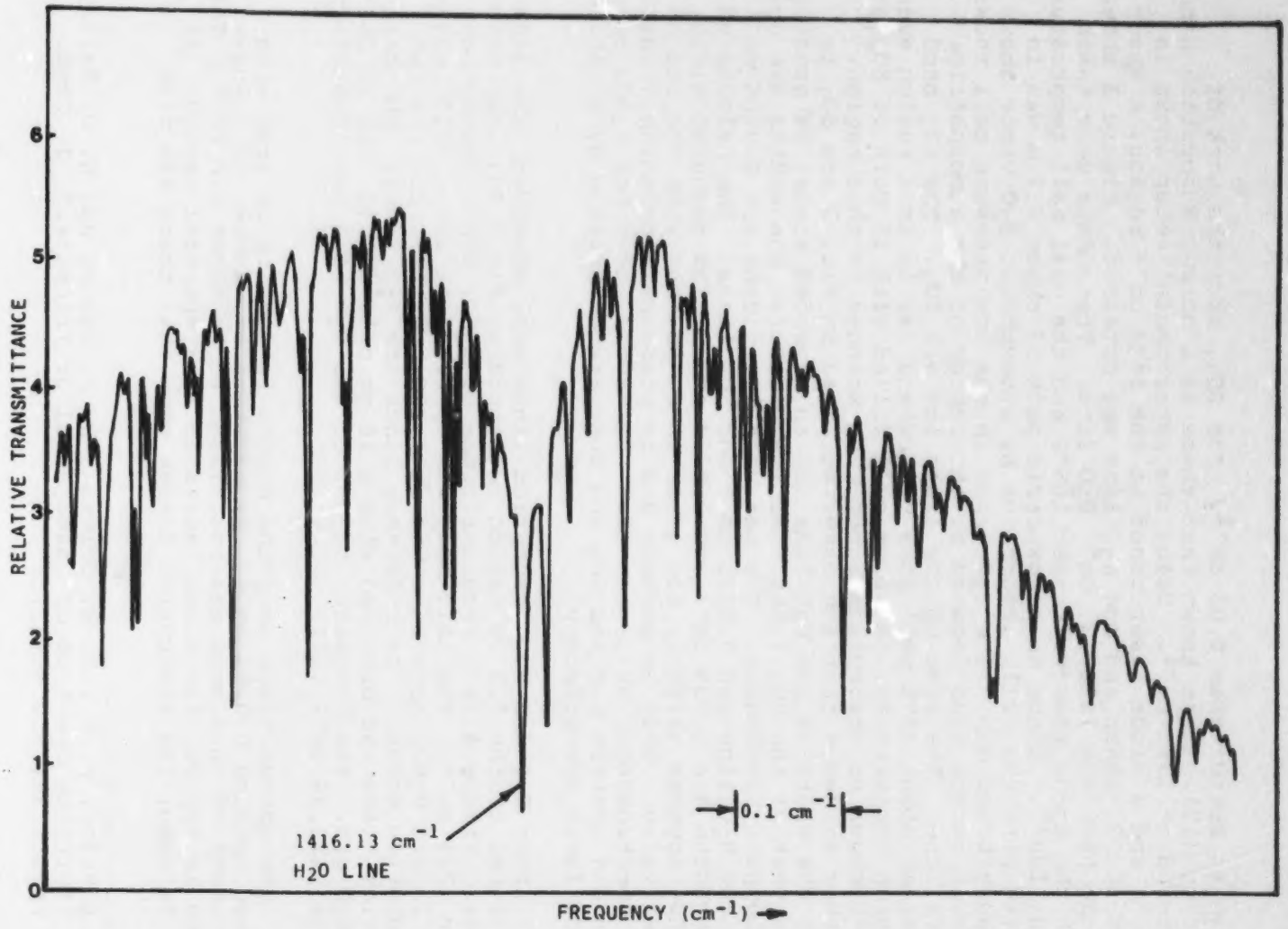

Figure 3. Absorption spectra above hot H_2SO_4 solution (T~165°C)

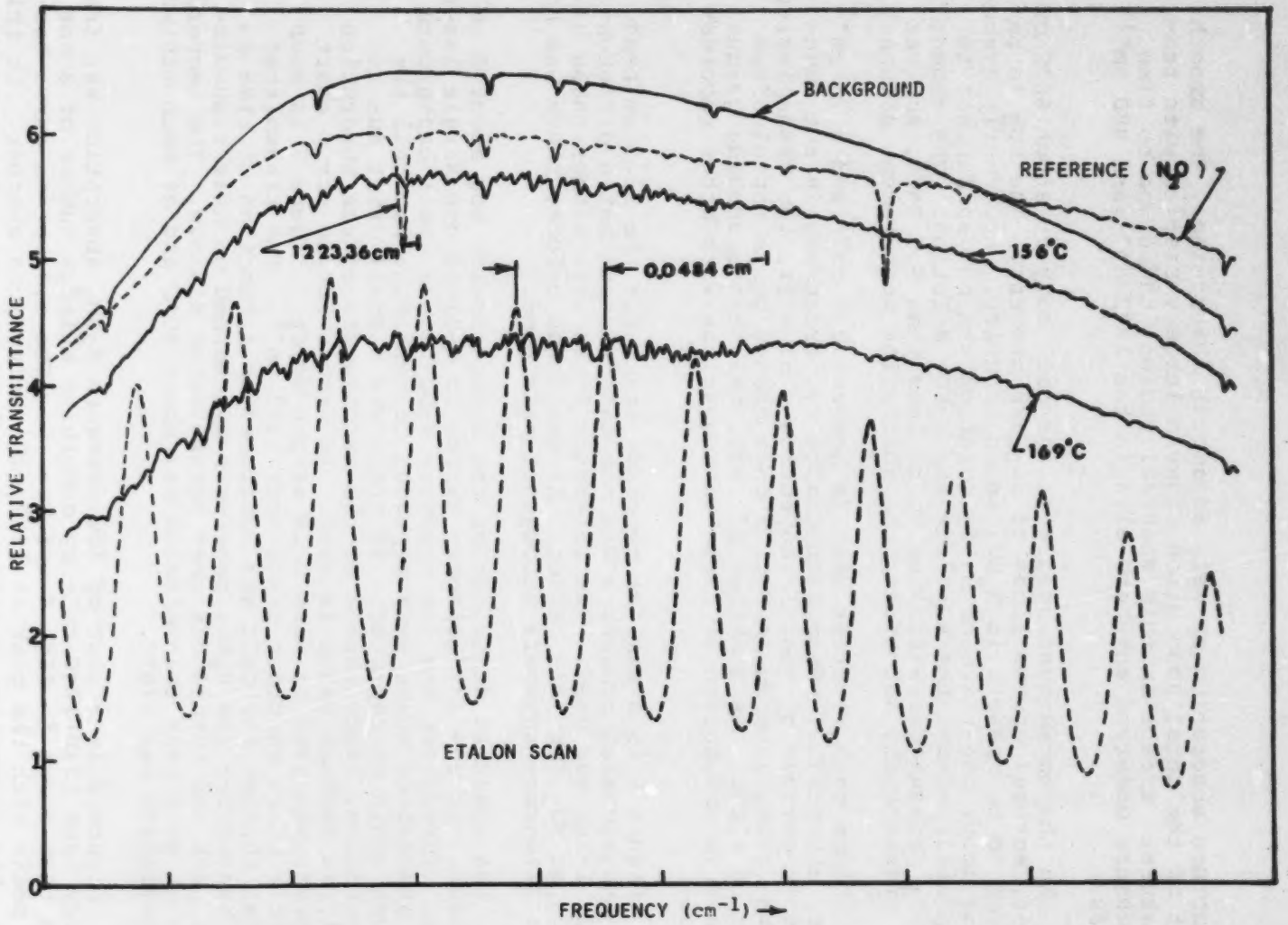

Figure 4. H_2SO_4 absorption near 1223 cm^{-1}

structure absorption as well as smooth absorption. The smooth part of the total absorption shows a large variation with temperature. Except in this spectral region, there was no fine structure observed anywhere else in the 1222 cm^{-1} and 880 cm^{-1} bands.

In the background scan with the cell body at about 60°C or lower, several narrow lines of SO_2 are present. The SO_2 is believed to be present in H_2SO_4 as an impurity. Apparently evacuating about one-third of H_2SO_4 solution was not sufficient to completely remove the SO_2 from the H_2SO_4 solution. The amount of SO_2 present was estimated to be less than 0.1 Torr, so that its presence did not affect the absorption measurement accuracy.

Since each recorder scan is between 0.5 cm^{-1} and 0.75 cm^{-1} wide, any gradual absorption change vs. frequency is not immediately obvious by visual inspection. However, the transmission in the range covered in Fig. 5 does change quite rapidly from left to right. As a matter of fact, this trace showing gradual change in absorption is large in comparison with other recorder traces.

Figure 6 is a similar recorder trace for the 11.3 μm band. The experimental procedure was the same except that a different diode laser was used. The reference lines were either those of $^{13}CO_2$ or NH_3 for this region. As mentioned before, there was no fine structure anywhere throughout this band.

The spectral slitwidth of the monochromator was about 2 cm^{-1} or less. It was sufficiently narrow to isolate one single laser mode. Throughout the low pressure H_2SO_4 scans, both background and absorption scans were repeated to determine how well the curves could be repeated. If there was a small drift due to electronics, laser source or the temperature of the absorption cell, an average value is used. In particular, a strip chart recorder was used to view this slight drift. Figure 7 is such a strip chart recorder trace near 1222 cm^{-1}. The transmitted signal through the cell was monitored as a function of time as the heater for the H_2SO_4 reservoir was turned on near transmission peak and turned off near transmission minimum. The temperature at each peak transmission was about 90°C and at each minimum transmission was 170°C.

Figure 8 is a plot of low pressure H_2SO_4 absorption vs. frequency from 1210-1240 cm^{-1} by combining a large number of scans like that shown in Fig. 4 and Fig. 5. The absorption curve has two peaks with the peak at 1222 cm^{-1} being much sharper. At this peak, the absorption coefficient is 7.2 cm^{-1}/atm. This compares with a value of 6.0 cm^{-1}/atm from Majkowski, which was measured at one atmosphere pressure of nitrogen and a value of about 4.0 cm^{-1}/atm from Burch, the H_2SO_4 pressure for which was not accurately known.

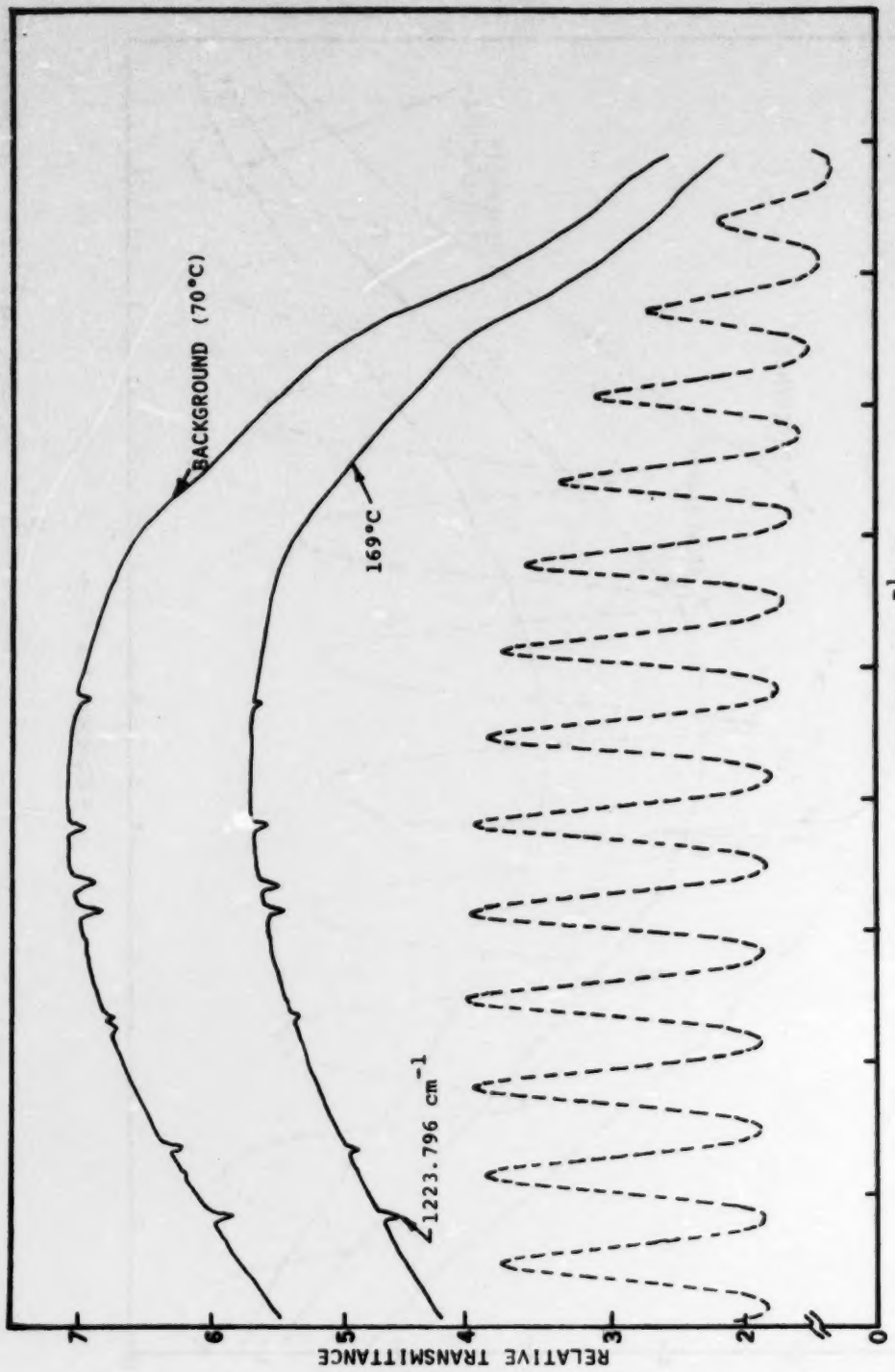

Figure 5. Low-pressure absorption H_2SO_4 absorption near 1224 cm^{-1}

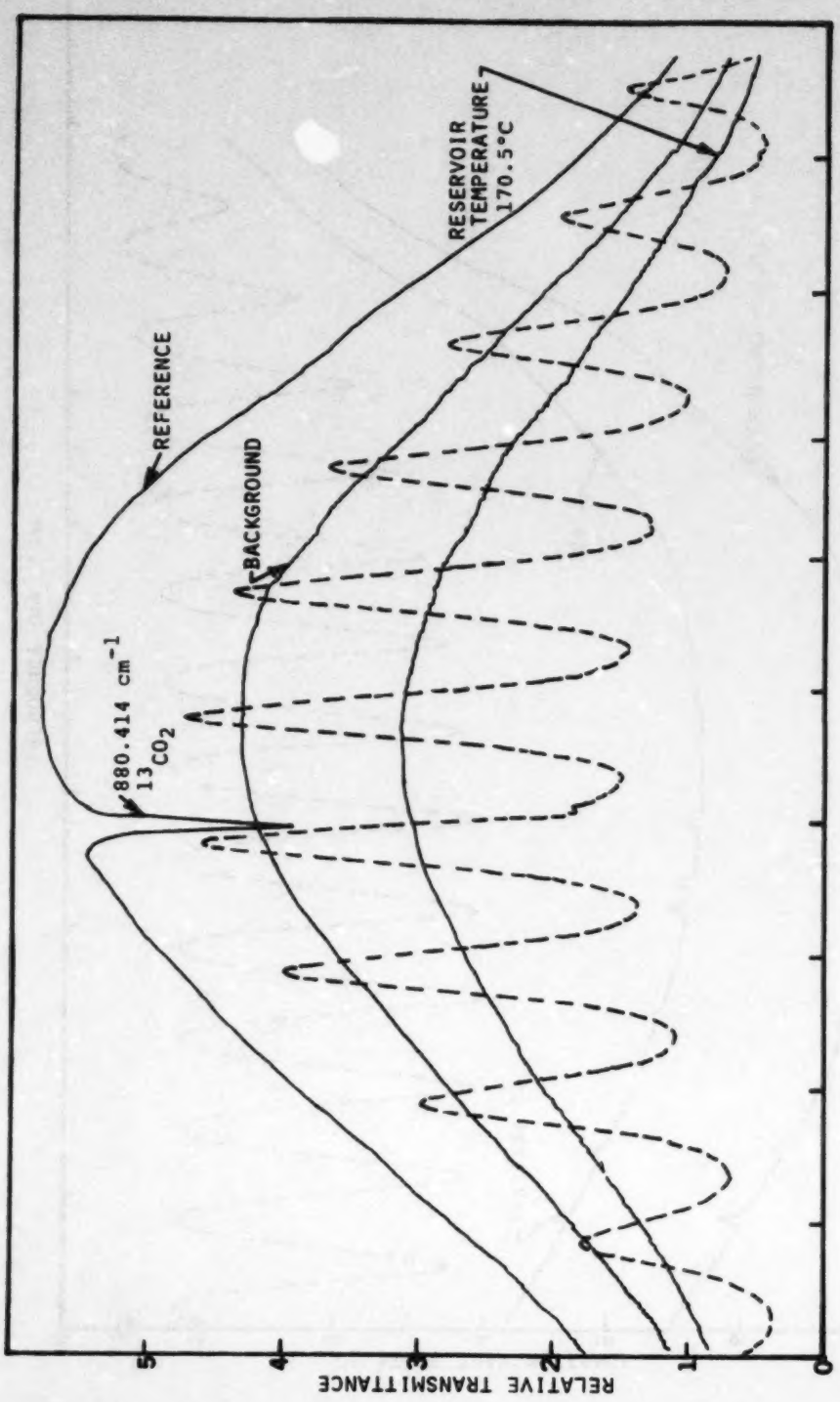

Figure 6. Low-pressure H_2SO_4 absorption near 880.5 cm^{-1}

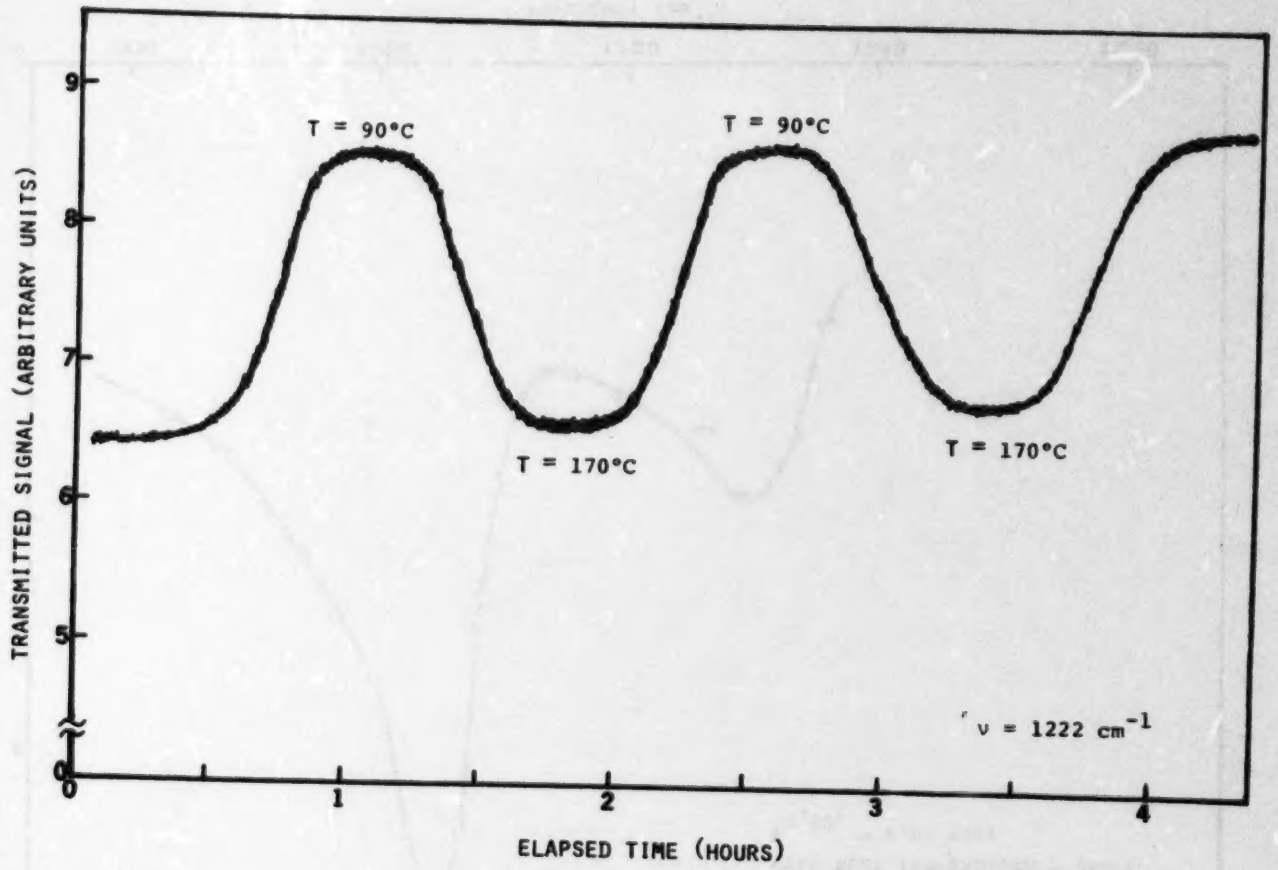

Figure 7. Strip chart recording of low pressure H_2SO_4 absorption vs. time

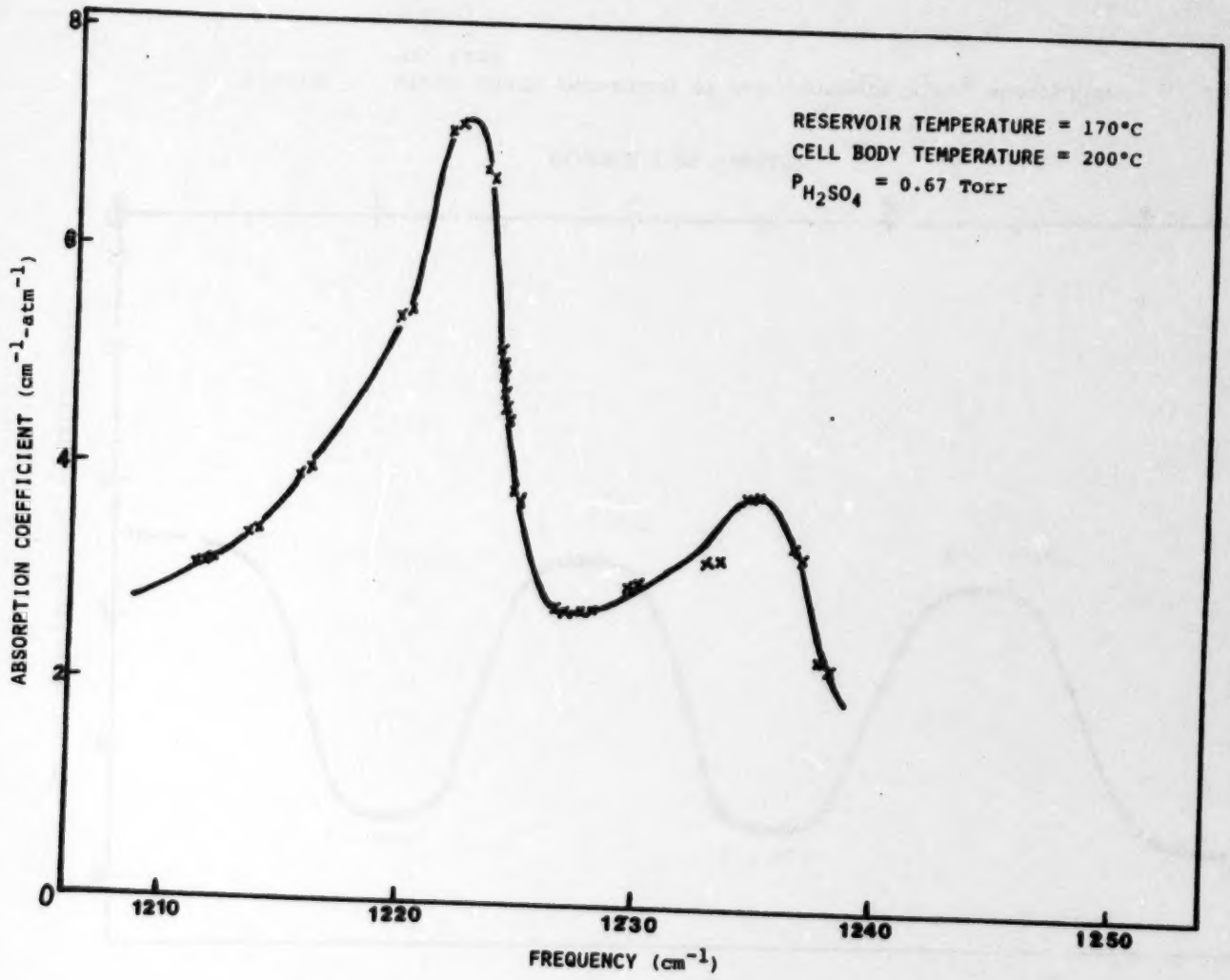

Figure 8. Low pressure H_2SO_4 absorption (P~0.67 Torr, T=170°C)

A similar plot was constructed for the 870-895 cm^{-1} region (see Fig. 9). There is only one peak. There was no sharp structure. The peak occurs at 880 cm^{-1} and is much broader in comparison with the peak at 1222 cm^{-1}. The absorption coefficient at this peak is about the same as that at 1222 cm^{-1} and is equal to about 7.0 cm^{-1}/atm.

HIGH RESOLUTION ABSORPTION MEASUREMENTS OF H_2SO_4 VAPOR IN ATMOSPHERIC PRESSURE OF NITROGEN

Experimental Apparatus and Methods

To perform the atmospheric scan, a different experimental setup with a different H_2SO_4 absorption cell was used. Figure 10 is a schematic diagram for the atmospheric pressure, flowing-gas H_2SO_4 vapor absorption measurements. With the exception of the absorption cell, the optical and electronic equipments are the same as those shown in Fig. 1. The flowing-gas cell is a transmission type. It has a window-to-window length of 64 cm. Again, wedged silicon windows were used and they were similarly sealed to the pyrex tube. Figure 11 is a detailed diagram of the flowing-gas H_2SO_4 absorption cell and the hot H_2SO_4 vapor generator. The inlet and outlet of the cell are closed to the windows to ascertain gas density uniformity throughout the cell. Thermocouples were attached to the cell wall at 10 cm intervals and to the cell windows. High temperature heating tapes were wrapped around the cell body with extra turns near the windows. The cell was placed inside a wood box, the inside surface of which was lined with heavy ceramic fiber cloth. Two salt windows were used to cover the openings on the box in order to minimize air convection and maintain a stable temperature operation around 230°C.

The H_2SO_4 vapor generator is similar to that used by Majkowski (7). A 15 cm^3 of 37N solution of reagent grade H_2SO_4 acid was introduced into the reservoir, which was then immersed in a heated oil bath. Dry nitrogen was used as a carrier gas at a flow-rate of about 1 liter/hr. The heat exchanger coil is a 6 mm O.D. pyrex glass tubing closely wound on a 37 mm O.D., 77 mm mandrel. The end of the pyrex coil extends into the H_2SO_4 reservoir and terminates in a glass frit (40-60 μm). The glass frit was necessary to obtain fine bubbling through the H_2SO_4 liquid and to prevent large aerosol from getting into the H_2SO_4 solution. At the outlet of the reservoir, quartz wool was used as a gas filter which allows only vapor to pass but prevents liquid aerosol from passing through. The oil bath used a high temperature oil (Dow Corning 200 fluid) which has a rather high flash point. However, it has a rather high viscosity even at 200°C so that constant stirring had to be applied to obtain a uniform temperature distribution throughout the bath. A thermocouple immersed in the bath forms part of a temperature control system.

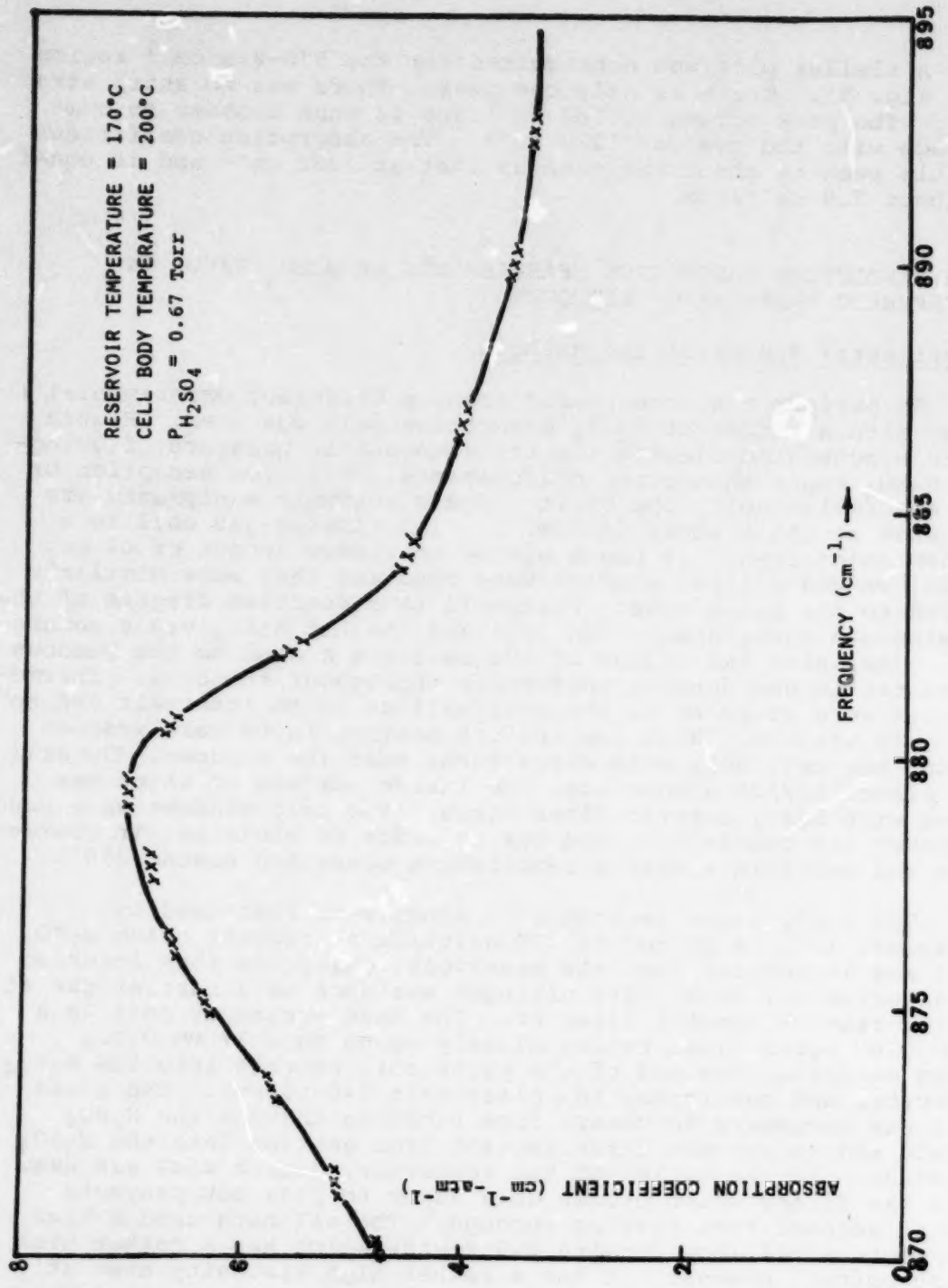

Figure 9. Low pressure H_2SO_4 absorption (P-0.67 Torr, T=170°C)

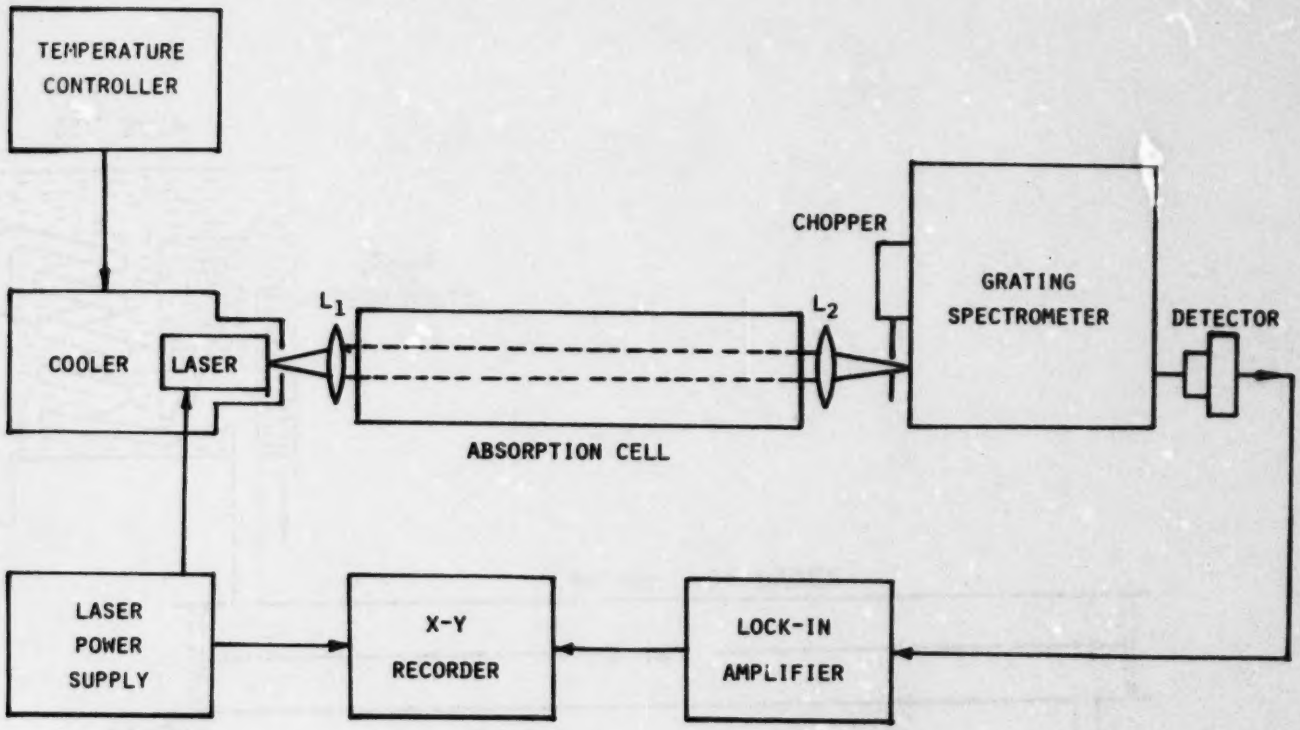

Figure 10. Experimental setup for H_2SO_4 absorption at atmospheric N_2 pressure

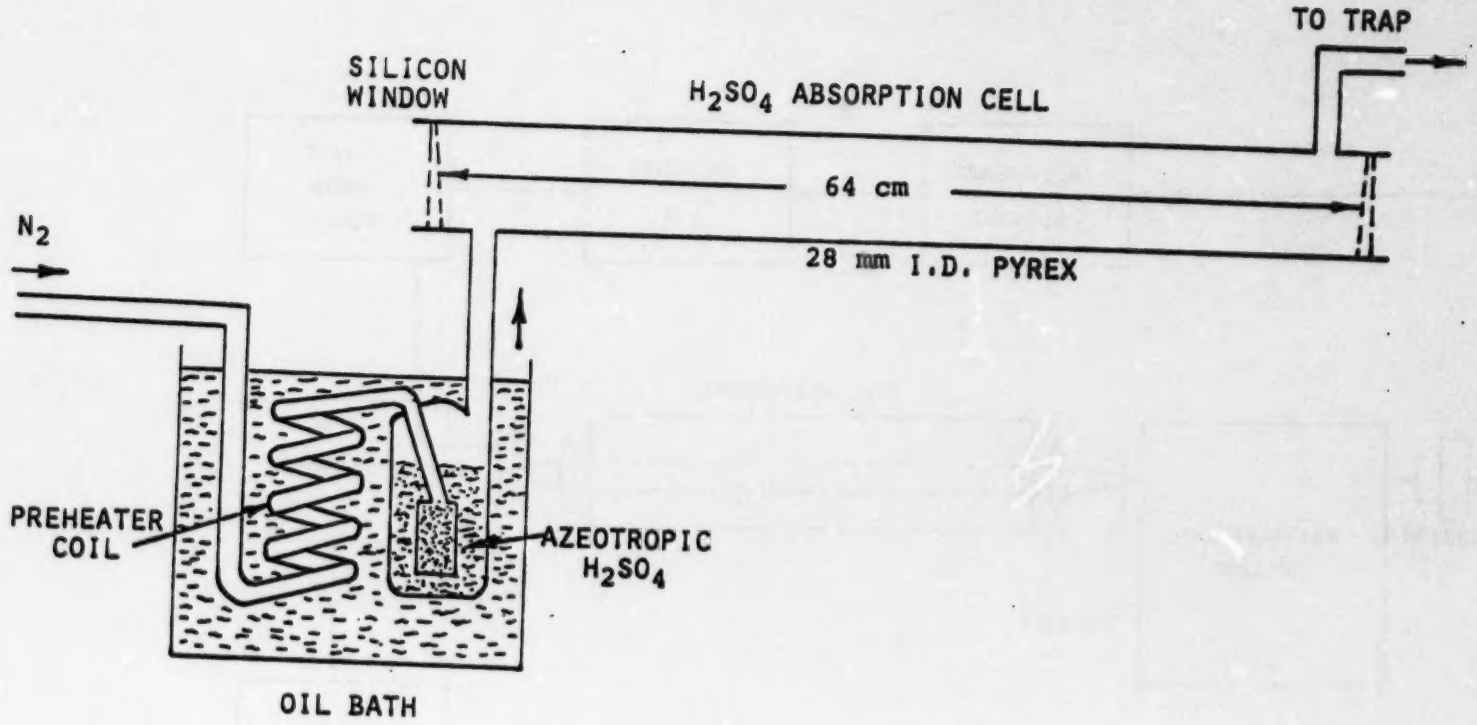

Figure 11. Absorption cell for H_2SO_4 absorption at atmospheric nitrogen pressure and H_2SO_4 vapor generator

In operation, the absorption cell body was kept at near 230°C and the oil bath at 180°C or at 200°C. The temperature at the connecting tube between the H_2SO_4 reservoir and the cell inlet was independently controlled to be as close to the bath temperature as possible. To achieve an azeotropic condition, the liquid H_2SO_4 was heated in the oil bath to 180°C and hot dry nitrogen was bubbling through the liquid for about 15 hours. At the end, only about 90% of the fluid remained in the reservoir. Since the 37N solution has an H_2SO_4 concentration of 98.9 ± 0.4% a 10% removal is believed sufficient in attaining the azeotropic condition (see page 13).

For a background scan, the reservoir temperature was lowered to about 60°C by cooling it with room air. Because the rate of dry nitrogen flow was about 1 liter/hr. and the volume of the cell was about 0.5 liter, sufficient time (~1 hour) was allowed after each reservoir temperature change before any data was taken. In practice, the equilibrium condition was noted by observing that the transmitted laser signal through the cell reached a steady-state value.

Experimental Results

Using the experimental setup for atmospheric pressure H_2SO_4 absorption measurements (see Fig. 10), the region from 1220 to 1222 cm^{-1} was scanned. The reasons that this particular 2 cm^{-1} region was selected are that the H_2SO_4 absorption peak occurs near 1222 cm^{-1} and that there is a very strong H_2O line near 1225 cm^{-1} which would present an interference problem. Figures 12 through 14 are the recorder traces. As in the low-pressure scans discussed earlier, for each spectral region, there are several traces vs. the same diode current, namely, background trace, etalon trace, reference trace, and absorption trace. As noted, there are two absorption traces, one at 180°C and the other at 200°C. The absorption vs. frequency profile is smooth. Since the recorder trace covers only about 0.5 to 0.7 cm^{-1}, about 3 or 4 similar scans are necessary to cover a 2 cm^{-1} continuous region. Figure 15 is a summary of the atmospheric scan data. The cell temperature was maintained at about 230 ± 10°C for both the 180°C and 200°C scans.

Since SO_2 have many lines in this 2 cm^{-1} region, it was used conveniently as frequency markers. The absolute frequency was determined by the H_2O line at 1220.320 cm^{-1}.

The absorption coefficients are given in units of 10^{-4} ppm^{-1}-m^{-1}. We have used the partial pressure spectroscopically determined in the present experiment (see section on partial pressure measurements, p. 42). At the peak absorption, 1222 cm^{-1}, points based on Majkowski's data and Burch's result (2 Torr of H_2SO_4 pressure) were also plotted. The 180°C absorption curve agrees within experimental error with Majkowski's

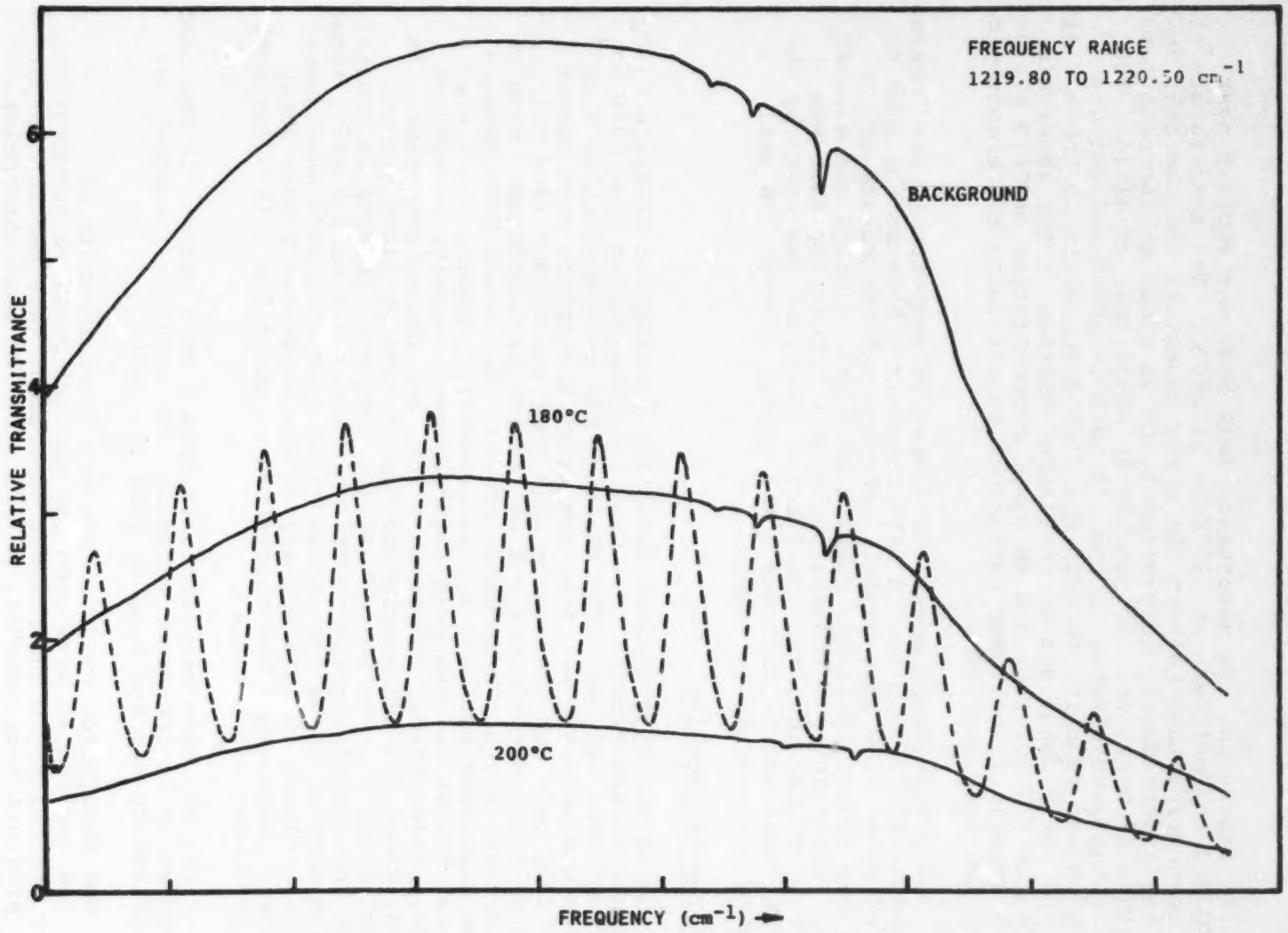

Figure 12. H_2SO_4 absorption at atmospheric nitrogen pressure

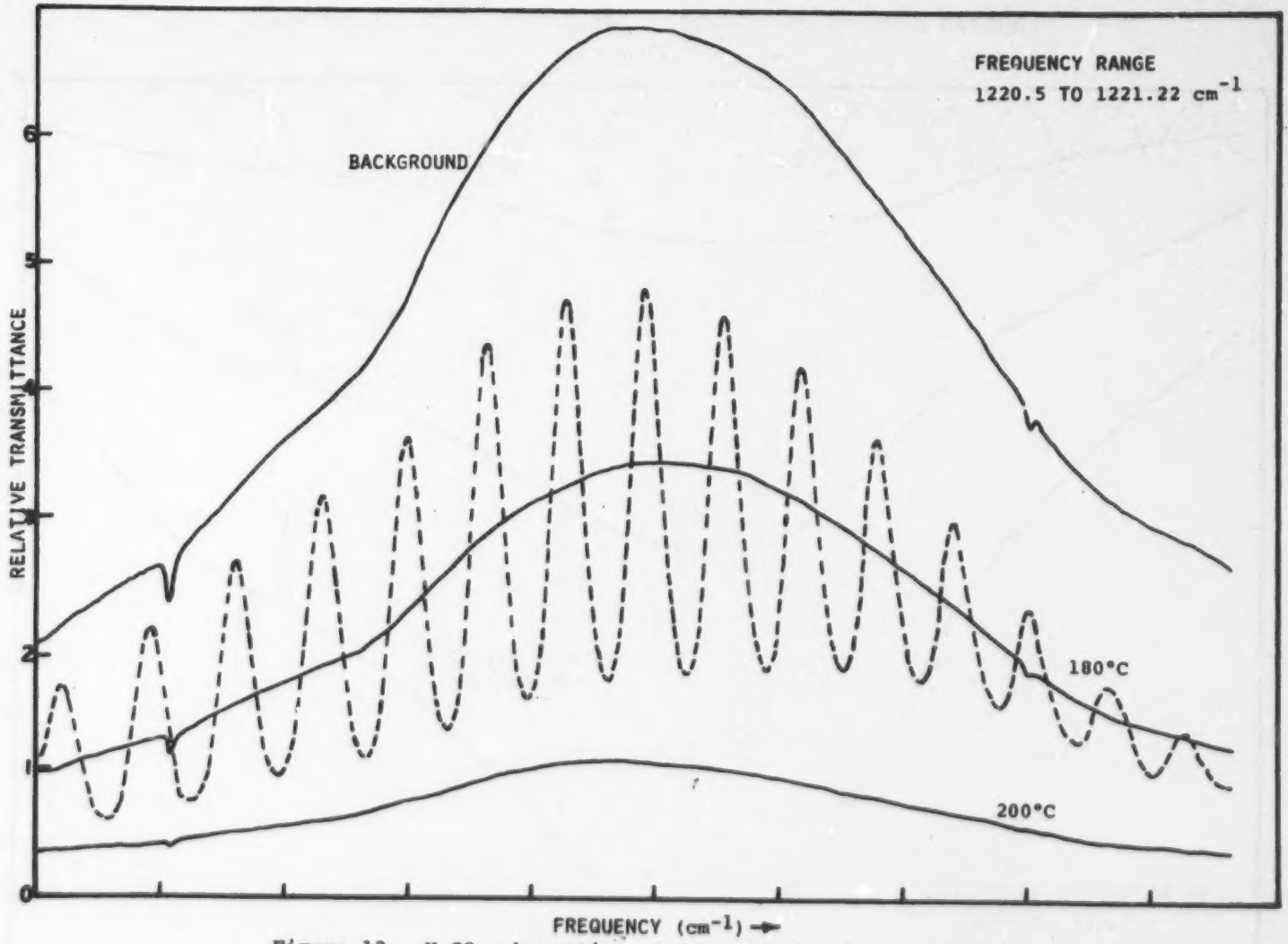

Figure 13. H_2SO_4 absorption at atmospheric nitrogen pressure

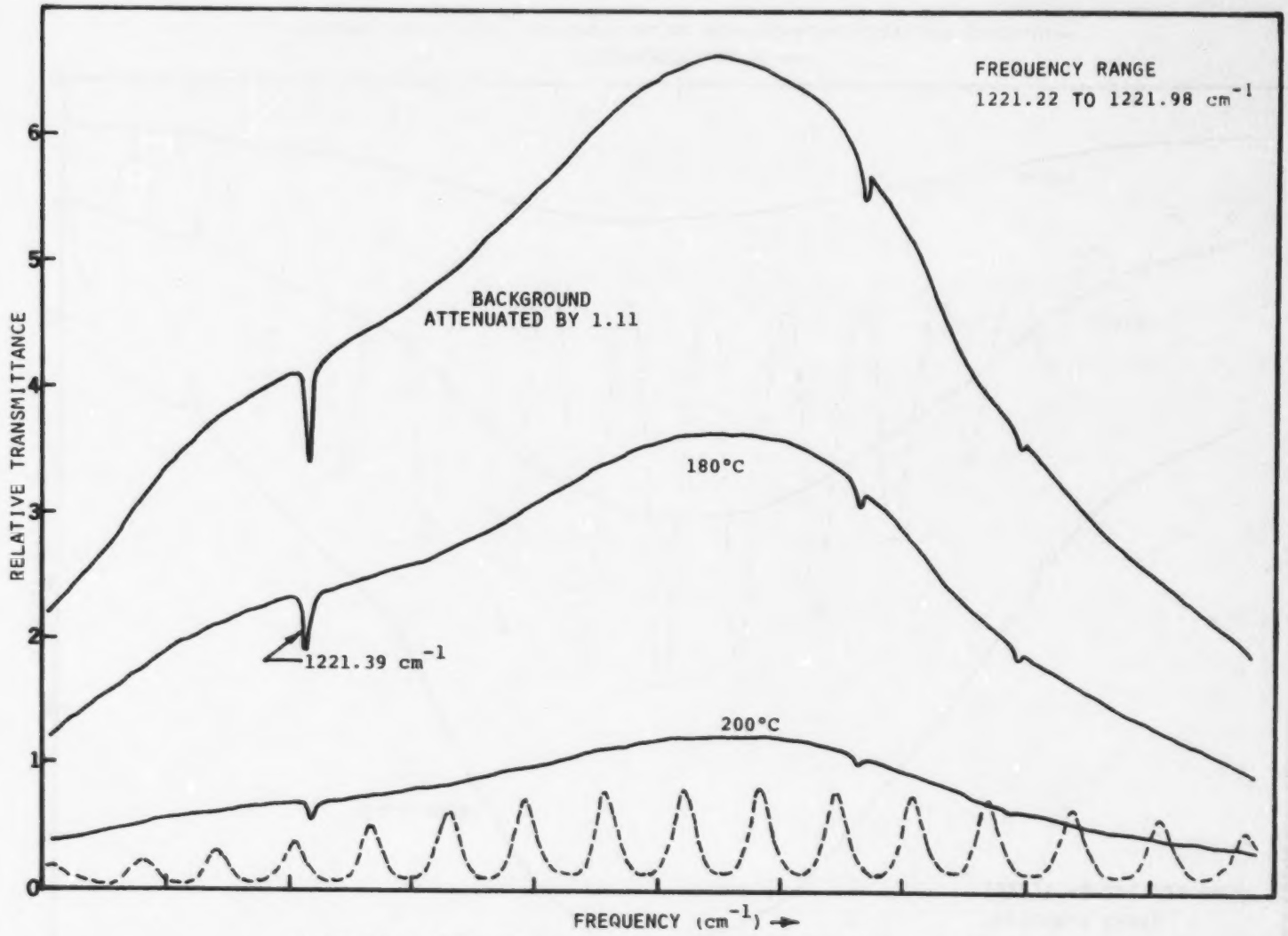

Figure 14. H_2SO_4 absorption at atmospheric nitrogen pressure

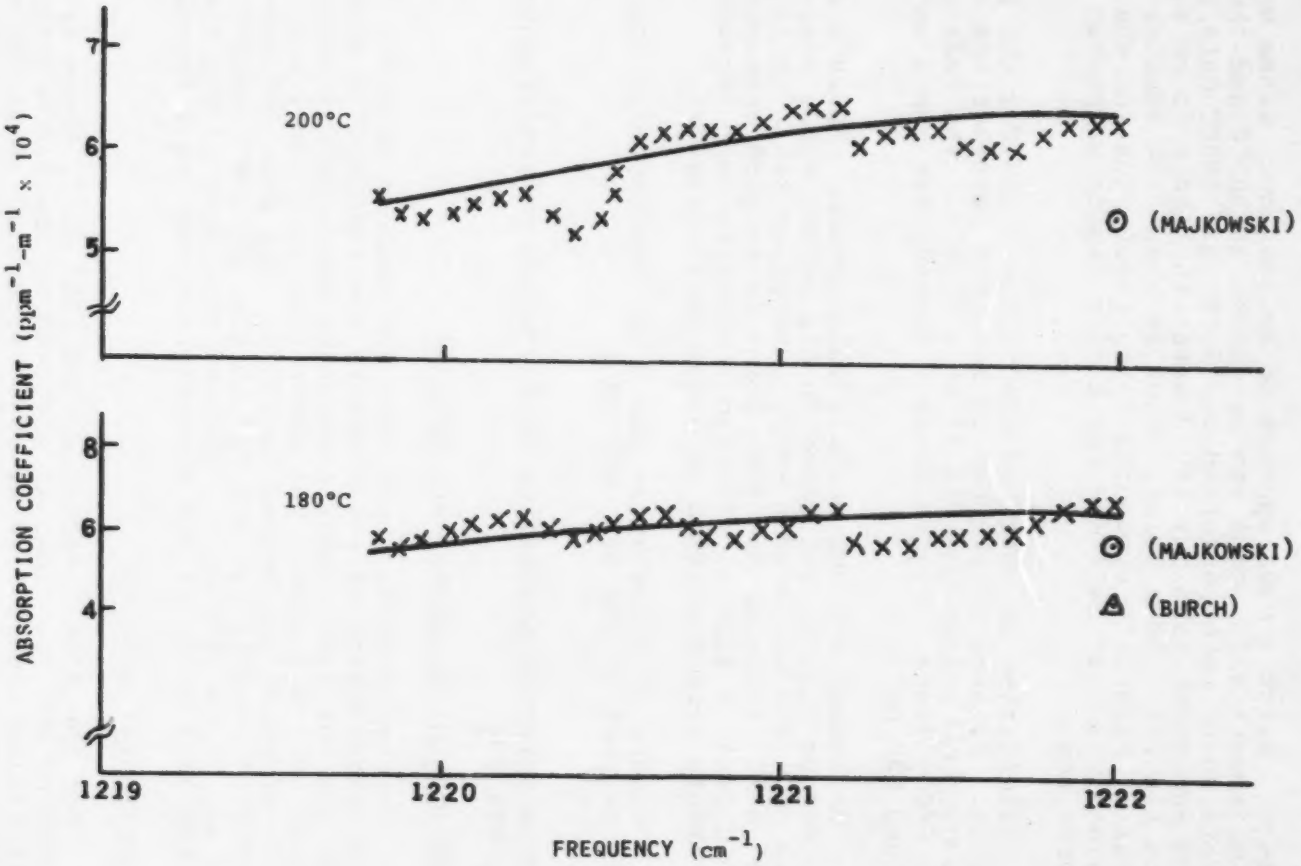

Figure 15. H_2SO_4 absorption at atmospheric nitrogen pressure

result. Burch's data appears to be too low. Since only one scan of Majkowski"s 25 scans was performed at 200°C and the majority of his scans were performed at 180°C, his 180°C data point (in good agreement with our 180°C data) is likely to be more accurate than his 200°C data point, which is about 15% smaller than our result. Figure 16 shows the H_2SO_4 absorption for the spectral region 1210-1240 cm^{-1} and the 2 cm^{-1} region we picked for atmospheric scan.

Similarly, we obtained absorption scans for the 880 cm^{-1} region. Figures 17 through 20 show the recorder traces covering the spectral region from 878.75 to 881 cm^{-1}. The reference lines are $^{13}CO_2$ lines. Figure 21 is a summary for the 2 cm^{-1} region around 880 cm^{-1}.

Majkowski did not measure this region. Burch's data point plotted on Fig. 21 was based on his 2-Torr H_2SO_4 measurement at 1222 cm^{-1} and his 3-Torr H_2SO_4 absorption ratio at 1220 and 879 cm^{-1}. Although his data point is in good agreement with our 180°C data, a direct comparison cannot be made because our measurements were performed at atmospheric pressure.

Figure 22 shows where the 2 cm^{-1} atmospheric scan is located with respect to the 880 cm^{-1} band.

HIGH RESOLUTION ABSORPTION MEASUREMENTS OF INTERFERANTS - H_2O, SO_2 AND CO_2

Experimental Apparatus and Methods

The experimental apparatus and methods used for the absorption measurements of interferants are exactly the same as those used for the H_2SO_4 vapor absorption measurements except that a larger cell was used. The absorption cell was 1.2 m long, only 1.1 m of which was heated to 200°C. The same reference gases were used, namely H_2O and N_2O in the 1222 cm^{-1} region and $^{13}CO_2$ and NH_3 in the 880 cm^{-1}. Because the lines of SO_2 are very dense in the 1222 cm^{-1}, it was conveniently used as a frequency marker.

Experimental Results

For the 2 cm^{-1} region around 1221 cm^{-1}, there are a large number of hot SO_2 lines as observed in the 1.2 m interference cell filled with 9 Torr of SO_2. Figure 23 shows one of several recorder traces in this region. Figure 24 is a summary plot of SO_2 absorbance vs. line position over a region about 3 cm^{-1} wide near 1221 cm^{-1}. It can be seen that the distribution of absorption lines are not uniform. Several strong peaks are present. Also, there are about four low-absorption regions, centered at about 1220.0 cm^{-1}, 1221, 1221.5 and 1222.1 cm^{-1}. For the same frequency region, a continuous absorption scan was also made

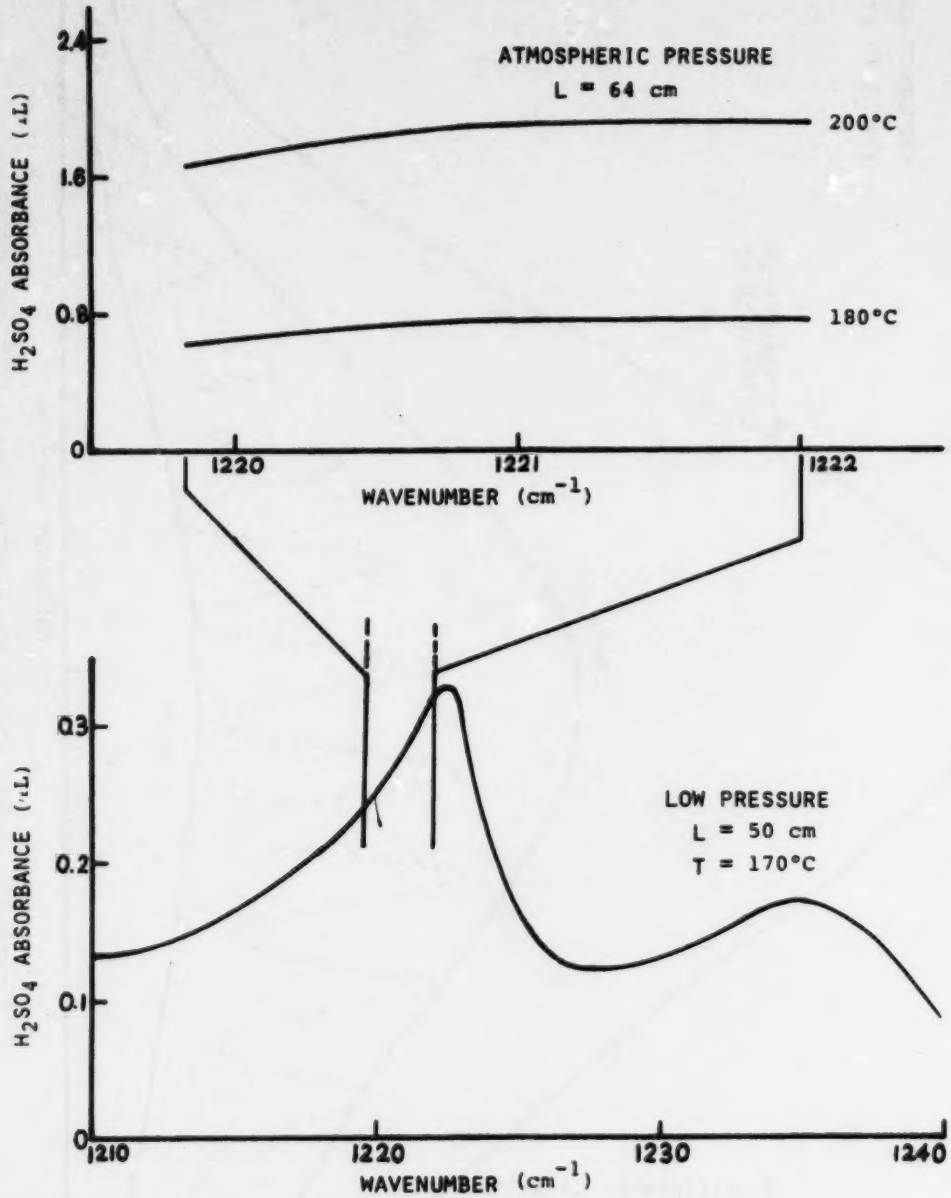

Figure 16. Location of the 2 cm^{-1} atmospheric scan region with respect to the 1210-1240 cm^{-1} low-pressure scan

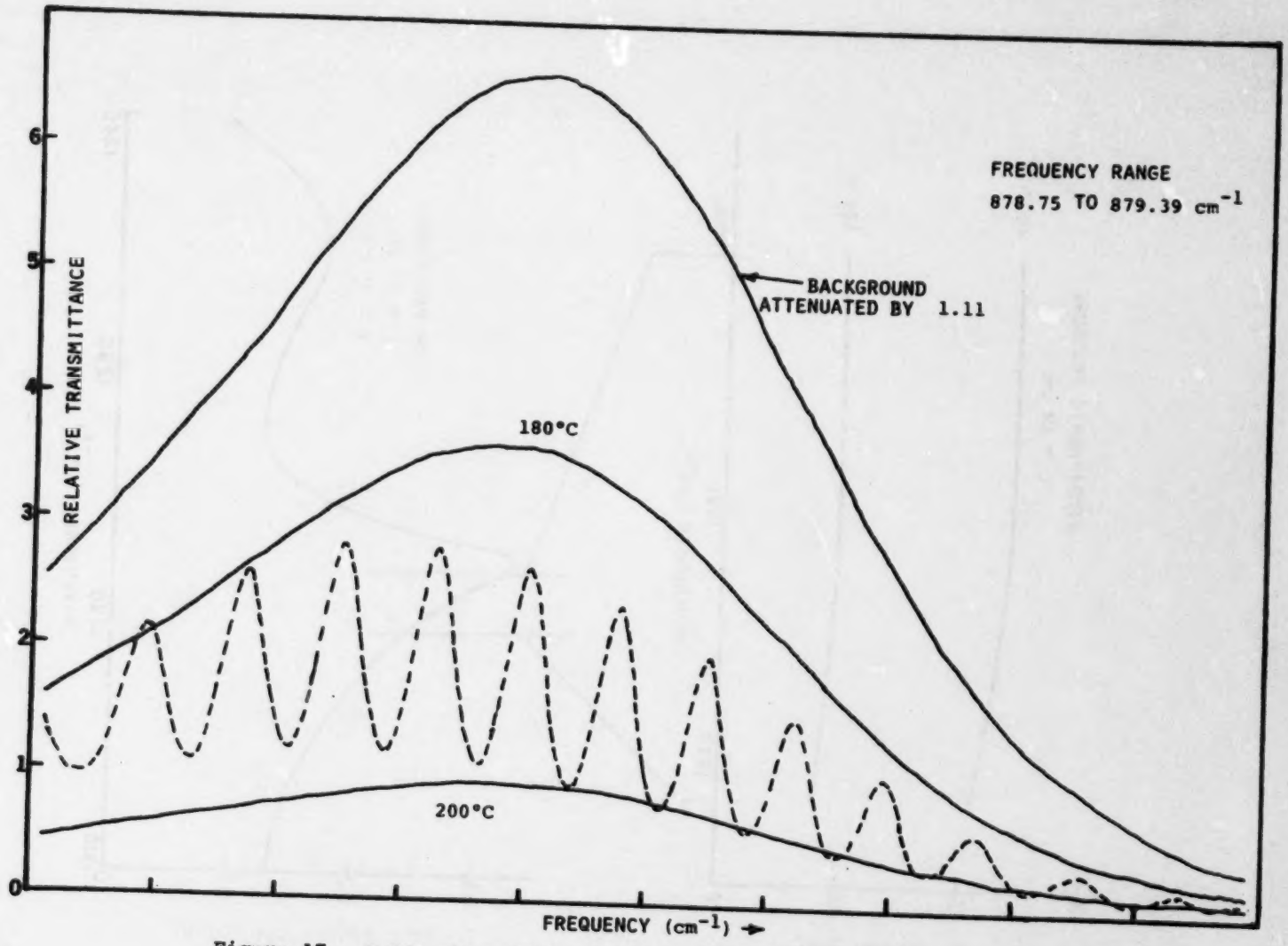

Figure 17. H_2SO_4 absorption at atmospheric nitrogen pressure

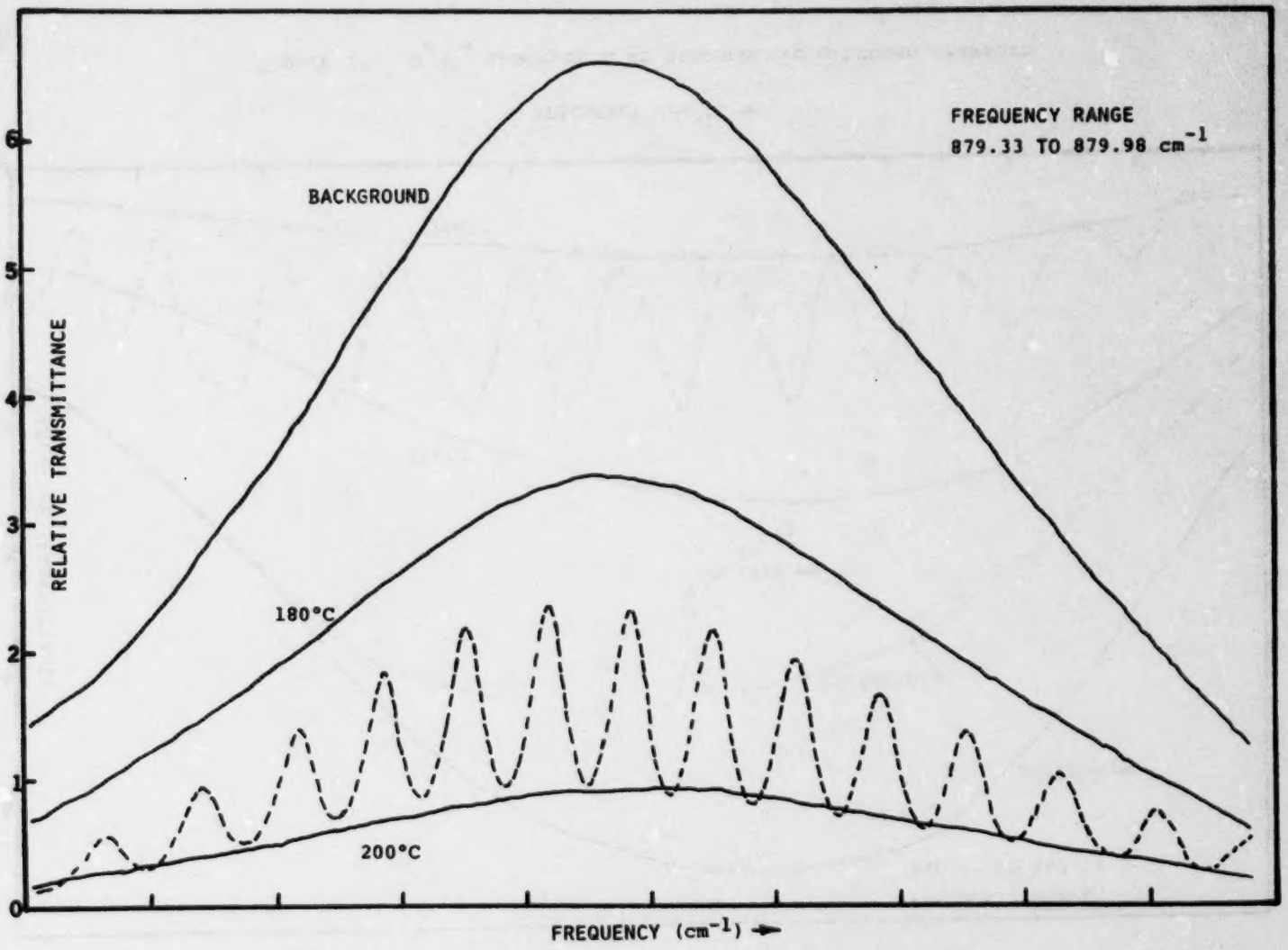

Figure 18. H_2SO_4 absorption at atmospheric nitrogen pressure

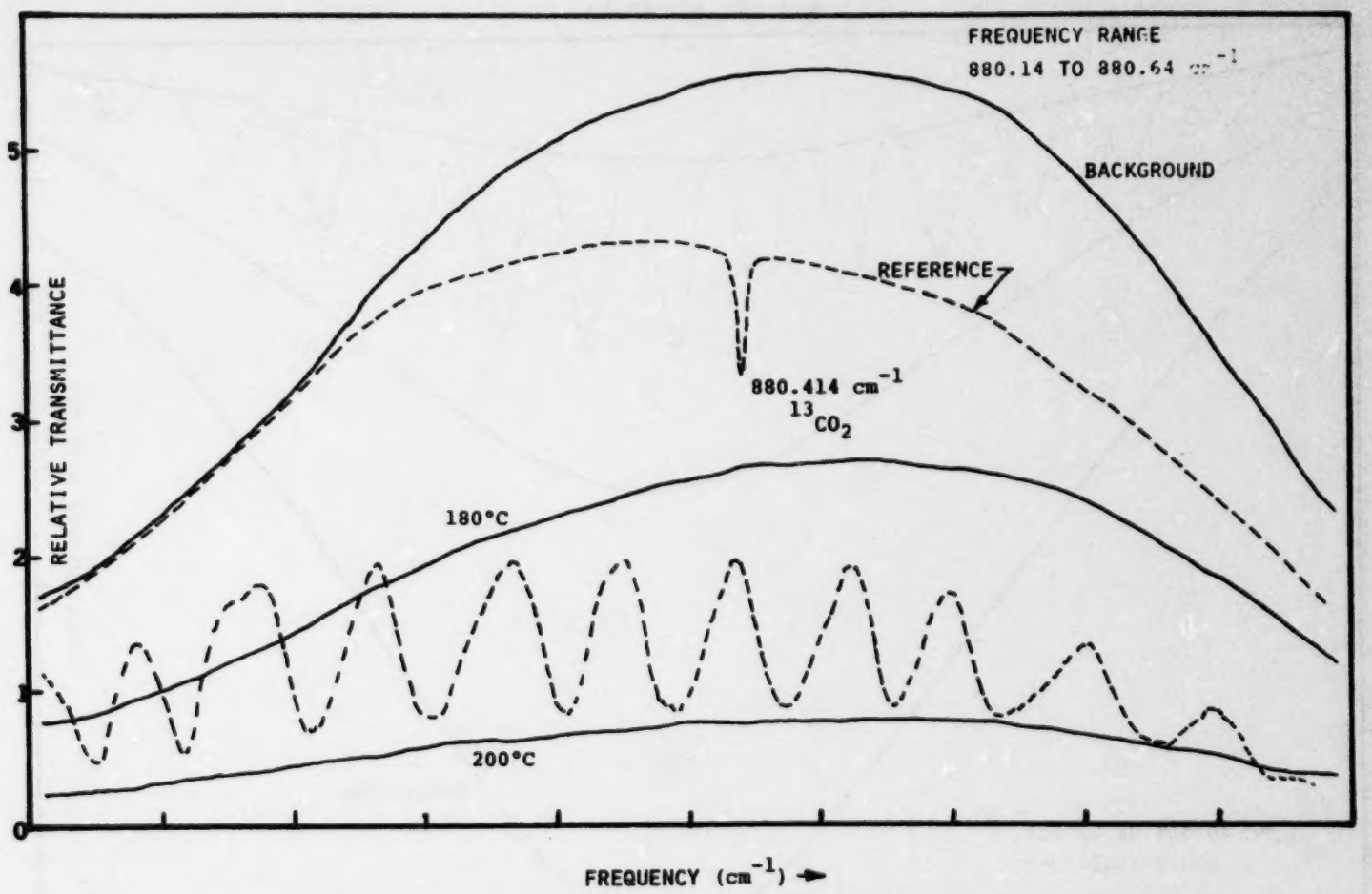

Figure 19. H_2SO_4 absorption at atmospheric nitrogen pressure

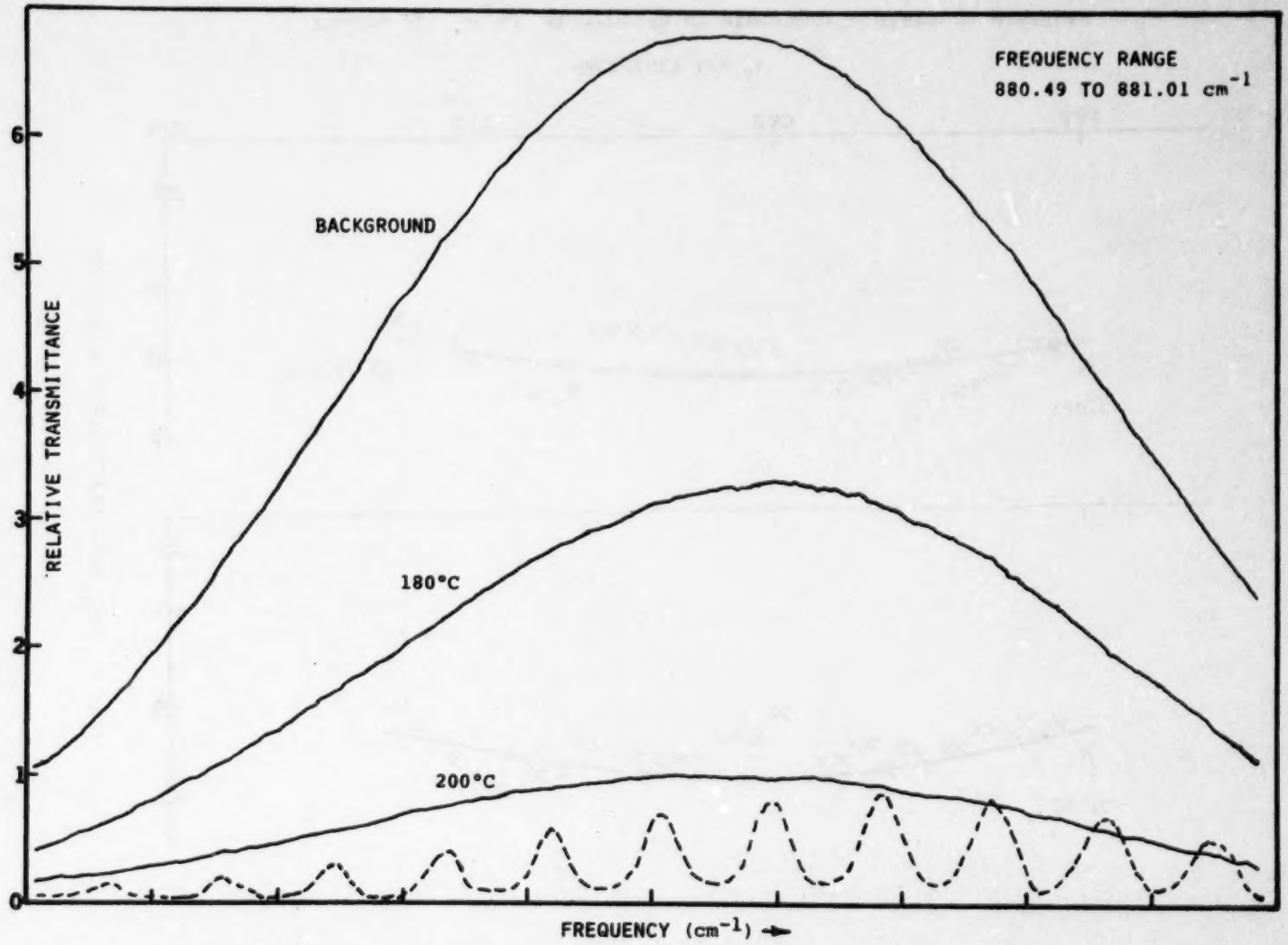

Figure 20. H_2SO_4 absorption at atmospheric nitrogen pressure

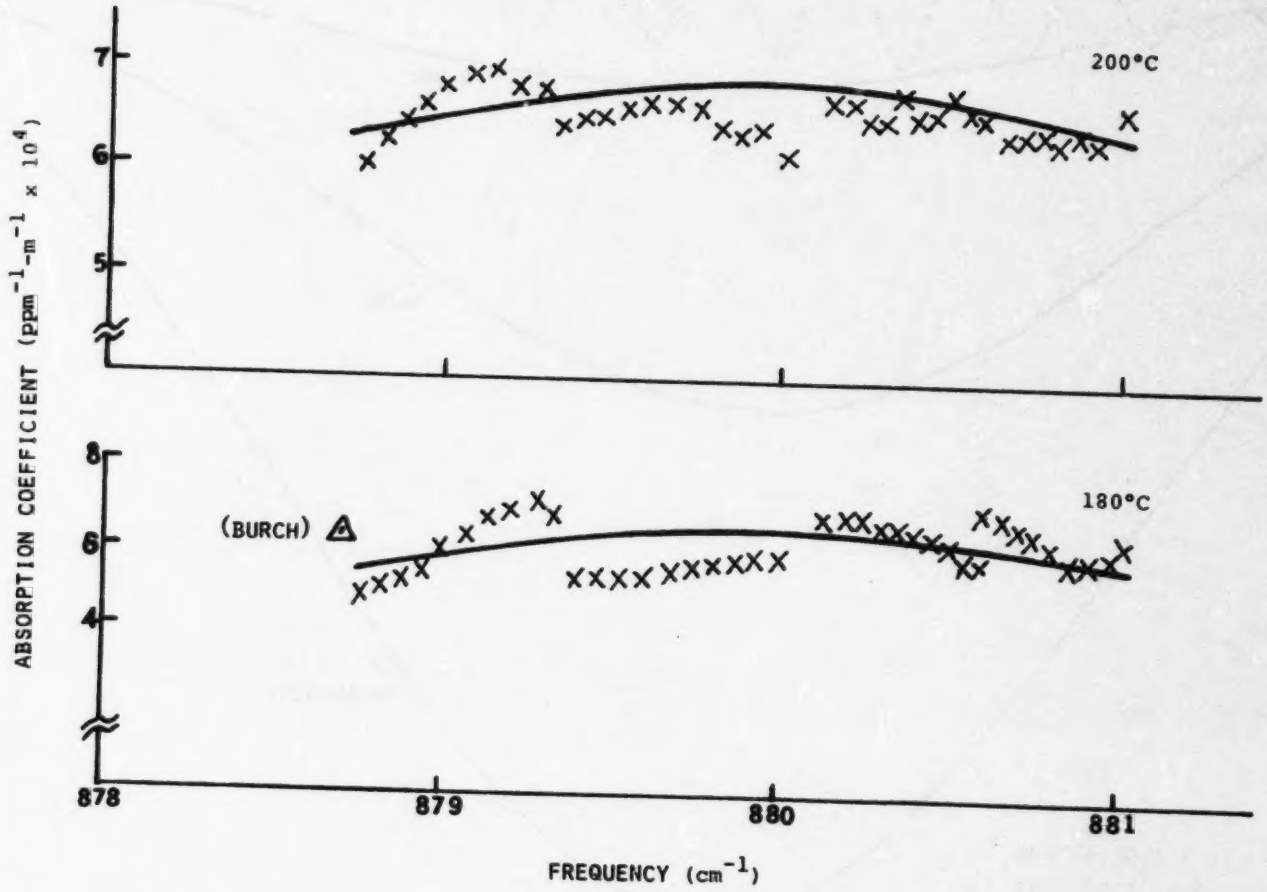

Figure 21. H_2SO_4 absorption at atmospheric nitrogen pressure

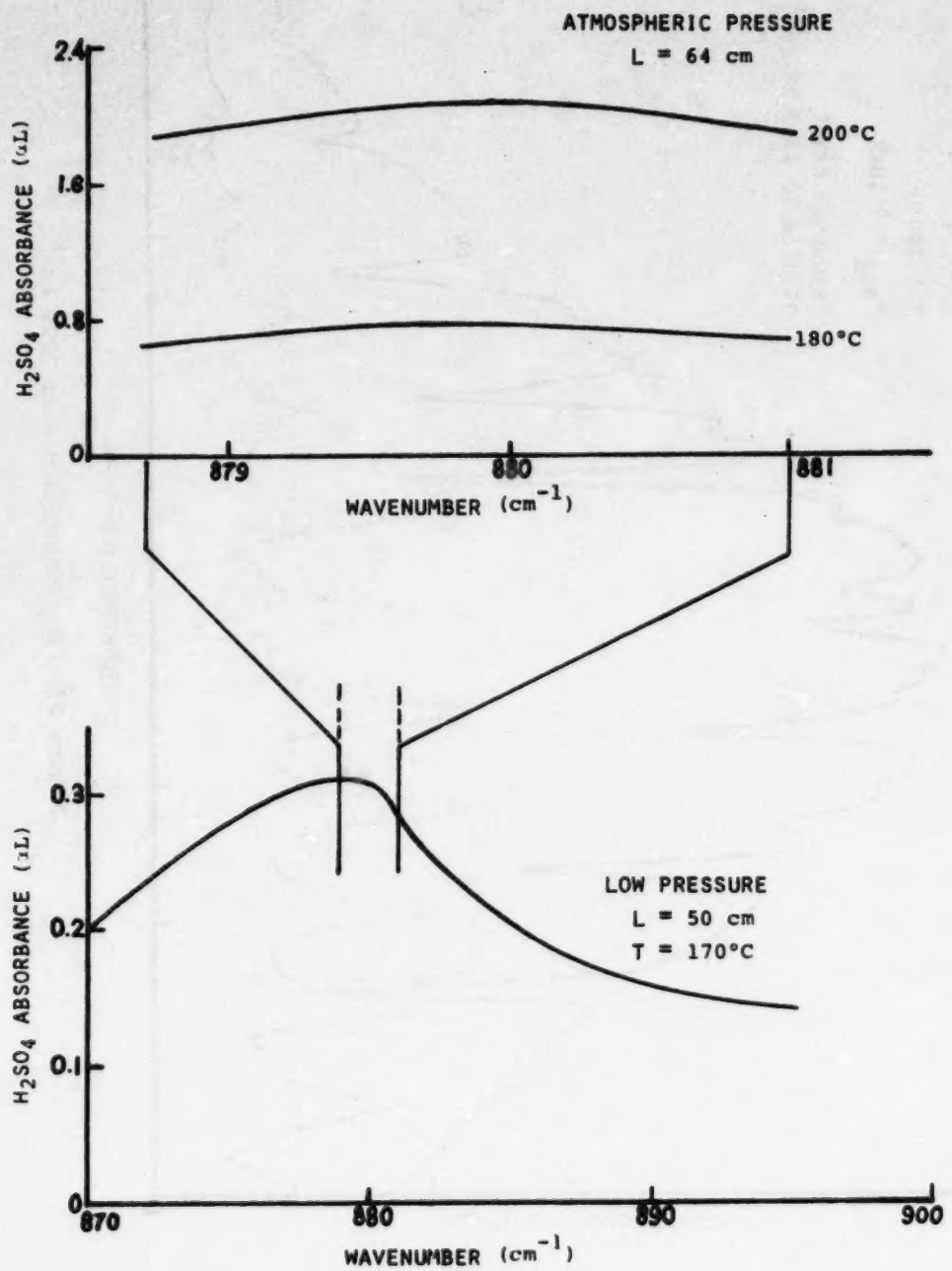

Figure 22. Location of the 2 cm^{-1} atmospheric scan region with respect to the 870-895 cm^{-1} low pressure scan

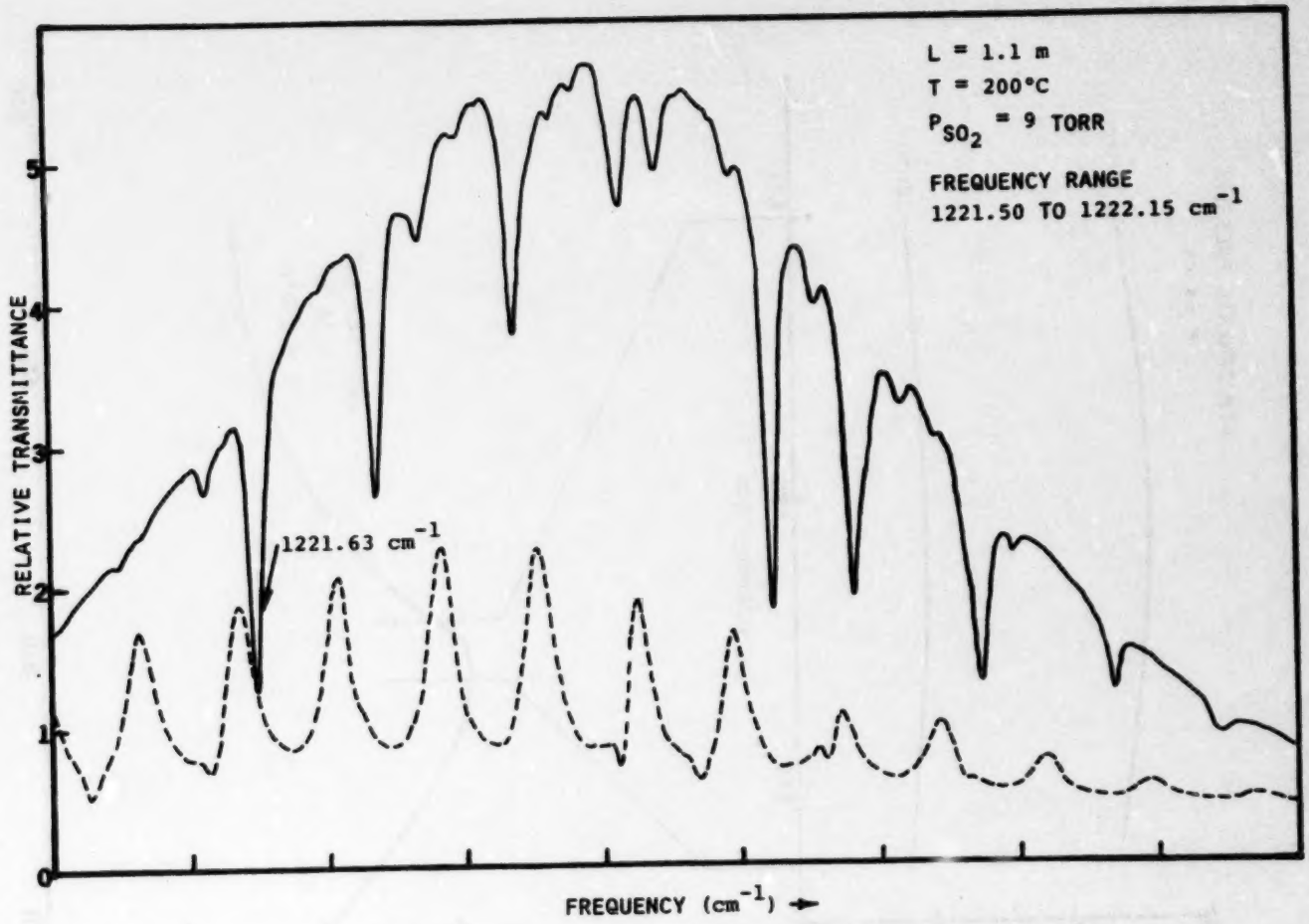

Figure 23. SO_2 absorption near 1222 cm^{-1}

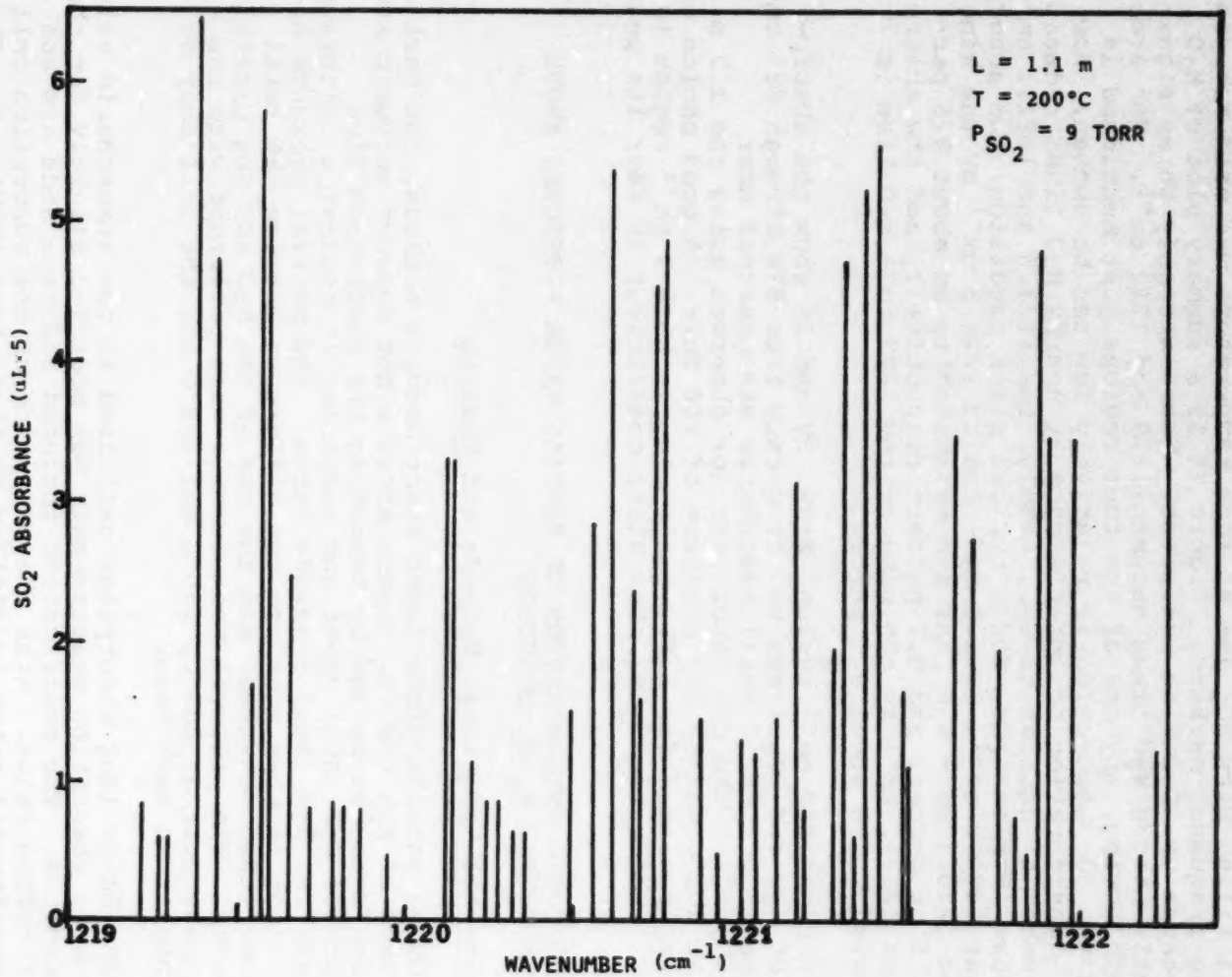

Figure 24. SO_2 absorption

using 10 Torr of H_2O in the same 1.2 m cell at 200°C. Figure 25 is a scan around 1220.320 cm^{-1} showing two H_2O absorption lines. A cell filled with SO_2 gas at room temperature was used for providing frequency markers. Figure 26 is a summary plot of H_2O absorbance vs. H_2O line positions. There are only three significantly strong H_2O lines between 1219 and 1222 cm^{-1}. For stack gas monitoring, any one of the four regions just mentioned in which the SO_2 absorption is relatively low can be chosen. However, consideration of interference by nearby H_2O lines reduces the number of choices to two, namely, the 1221.5 and 1222.1 cm^{-1} regions. For example, for a typical stack condition, the absorption at 1220.0 cm^{-1}, 1221.0 cm^{-1} and at 1221.5 cm^{-1} by the wing of the 1220.3 cm^{-1} H_2O line are estimated to be about 2.5 percent, 0.56 percent and 0.2 percent respectively, and the absorption at 1222.1 cm^{-1} by the wing of the 1225 cm^{-1} H_2O line is estimated to be about 0.1 percent.

For the 880 cm^{-1} region, Figs. 27 and 28 show the absorption of H_2O and CO_2 lines vs. frequency from 878 through 881 cm^{-1}. Only one H_2O line of small absorbance was observed near 878.56 cm^{-1}. The CO_2 lines were not observed using the 1.2 m cell at 200°C with a CO_2 pressure of 100 Torr. A good choice of spectral position for H_2SO_4 monitoring in this 3 cm^{-1} region is 880 cm^{-1} where the H_2SO_4 absorption coefficient is near its peak.

SPECTROSCOPIC DETERMINATION OF PARTIAL VAPOR PRESSURES ABOVE HOT AZEOTROPIC H_2SO_4 SOLUTION

Experimental Apparatus, Methods and Results

Using tunable diode laser spectroscopic methods, the partial pressures of H_2O and SO_3 vapors above a hot aqueous sulfuric acid solution were determined by measuring the absorption line strength of H_2O (SO_3) vapor and comparing it against a calibrated strength vs. H_2O (SO_3) pressure curve. The partial pressure of H_2SO_4 vapor is then equal to the difference between the total pressure (also measured) and the sum of the H_2O and SO_3 partial pressures. The pressure measurements were performed with the H_2SO_4 reservoir at 107°C, 150°C and 200°C and the cell body at 20°C higher in each case.

The 64-cm long absorption cell used in the atmospheric sulfuric acid absorption measurements was modified slightly for the measurements. The modification included adding a side arm and an all-teflon valve. With the exception of the absorption cell the experimental setup is similar to that shown in Fig. 1. The following paragraphs describe the methods and results of the measurements.

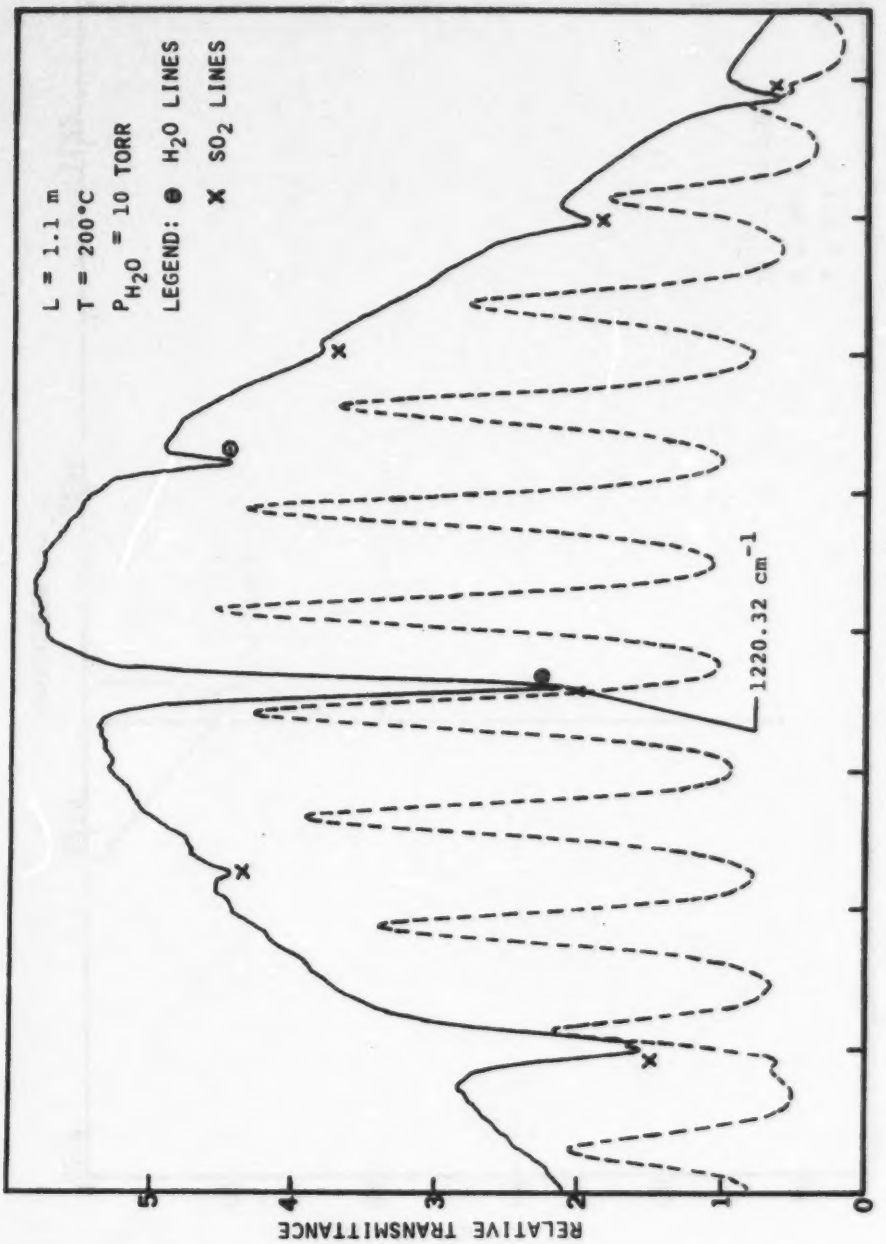

Figure 25. H_2O absorption

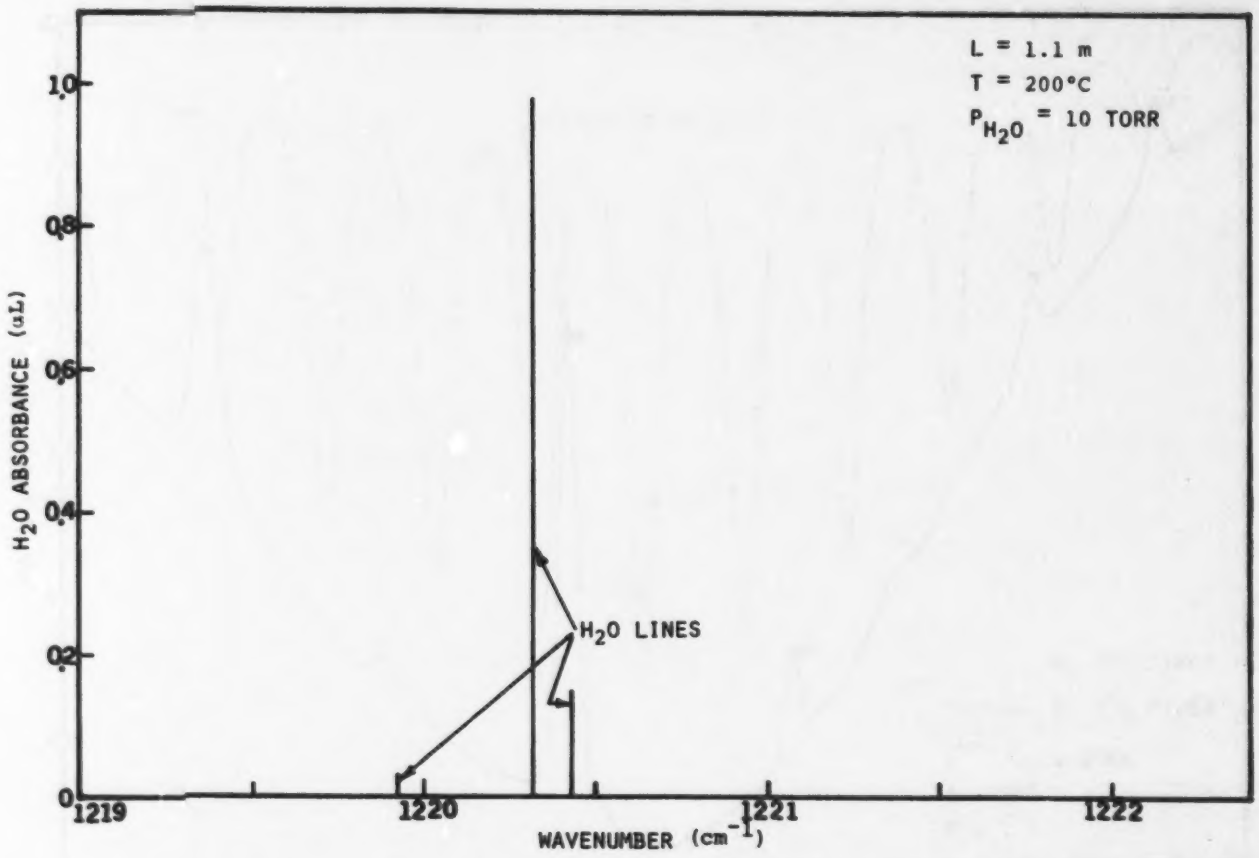

Figure 26. H_2O absorption

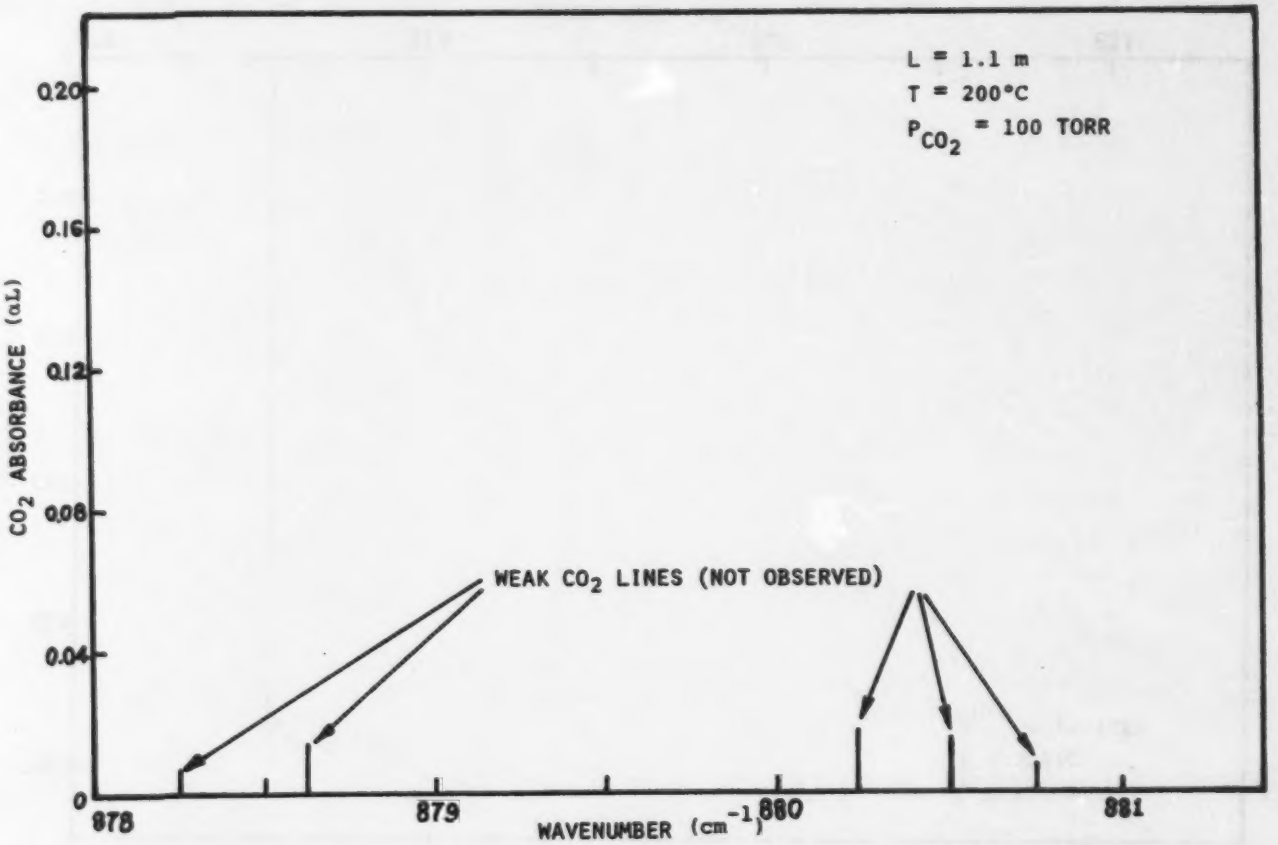

Figure 27. CO_2 absorption

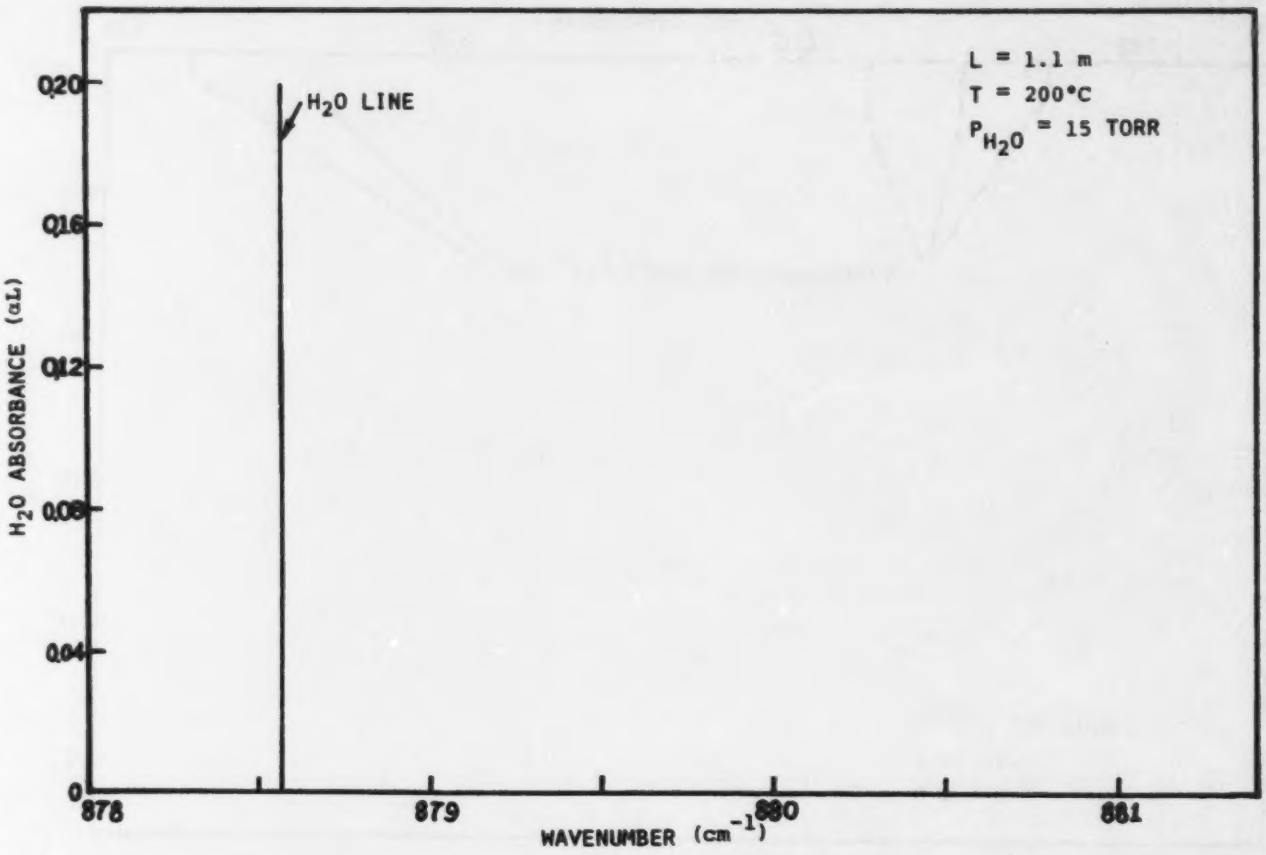

Figure 28. H_2O absorption

H_2O Partial Pressure Measurements--

The modified cell was used for both the absorption strength measurements and the calibration measurements. In the calibration measurements, a few cm^3 of distilled H_2O was placed in the side arm which was then immersed in saturated brine solution at about -19°C. At this temperature the water vapor pressure is about one Torr. The absorption strength of an H_2O line at low pressure near 1330 cm^{-1} was measured at a number of cell body temperatures by tuning a diode laser through the line. Figure 29 is a plot of the absorbance per Torr of H_2O pressure vs. cell body temperature. After obtaining the calibration curve, the water in the side-arm was replaced by an H_2SO_4 azeotrope and an absorption scan was obtained. Figure 30 is a recorder trace of the same H_2O absorption line above 150°C H_2SO_4 azeotrope. The azeotrope was prepared by distilling off about one third of a 37N H_2SO_4 at the azeotrope temperature. By comparing the absorption strength of the line in Fig. 30 with the calibration curve in Fig. 29, the partial pressure of H_2O was determined to be about 0.23 Torr. That is, for a 150°C azeotrope (side arm temperature)

$$P_{H_2O} = \frac{\alpha L(\text{calculated from Fig. 30, } T_{body} = 170°C)}{\alpha L/P_{H_2O}(\text{from Fig. 29 at } T_{body} = 170°C)}$$

Azeotrope at other temperatures were prepared and the partial pressures were determined similarly. Table 1 summarizes the H_2O partial pressure measurement results. The numbers in parenthesis are from Luchinskii for the atmospheric azeotrope with a 98.3% H_2SO_4 concentration (9).

SO_3 Partial Pressure Measurements--

For the SO_3 partial pressure measurements the same absorption cell used for the H_2O partial vapor pressure measurements was used. The SO_3 was purchased from a commercial source with a stated purity of 99%. Because of the much higher vapor pressure (14), the side arm was immersed in a methanol-water mixture at about -40°C (~1 Torr of SO_3 vapor pressure) for the calibration runs. Figure 31 is the plot of absorbance per unit pressure vs. temperature for an SO_3 line near 1354 cm^{-1}. Figure 32 is a recorder trace of the same SO_3 line above a 150°C H_2SO_4 azeotrope. Table 2 is a summary of the SO_3 partial pressure measurement results. Again, the numbers in parenthesis are from Luchinskii. It can be seen that the SO_3 pressure is much higher than that of the 98.3% azeotrope.

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14. Handbook of Chemistry and Physics, 46th Ed. 1964, p. D101, The Chemical Rubber Col, Cleveland, Ohio.

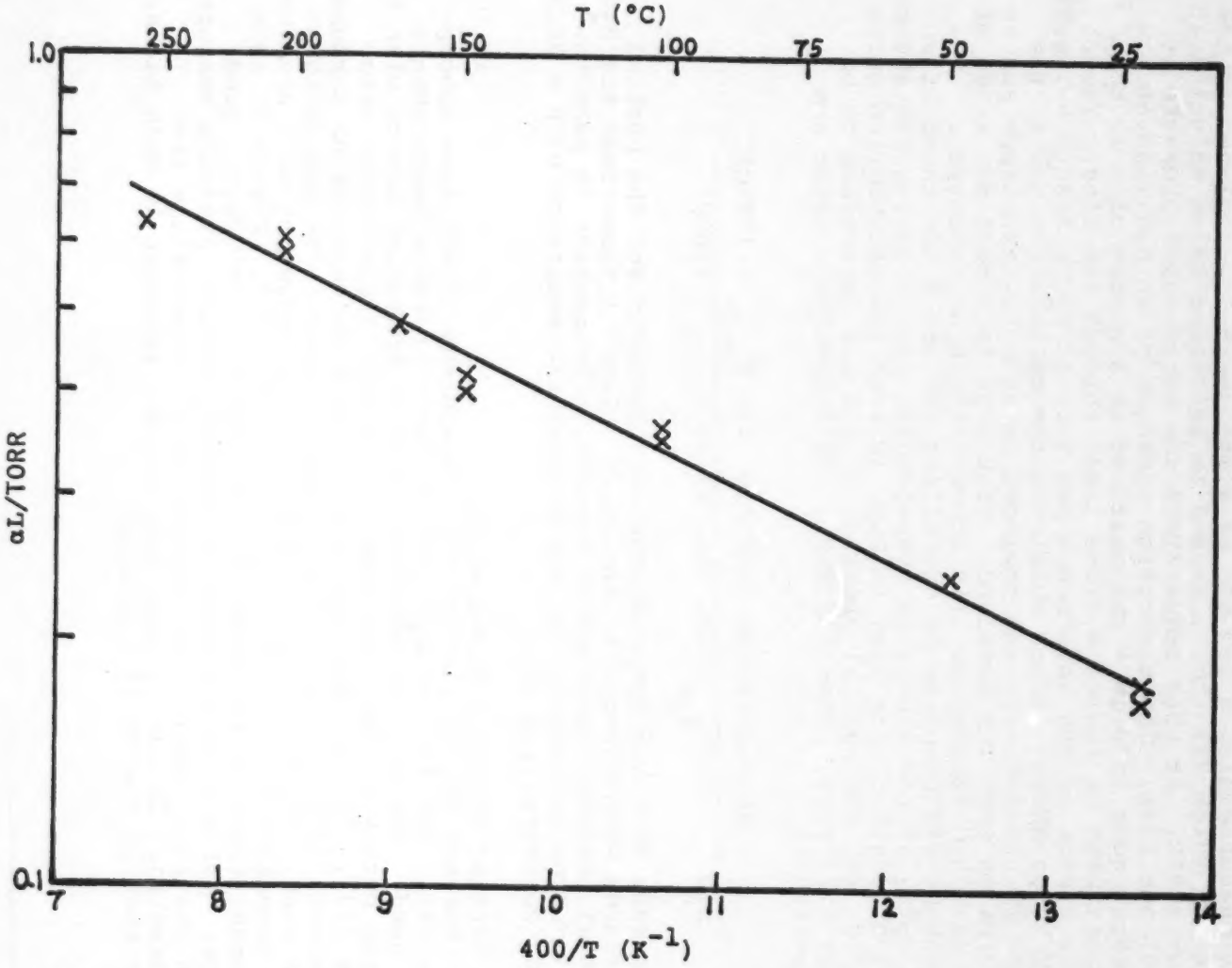

Figure 29. Absorbance per unit pressure (αL/Torr) vs. temperature of cell body for the H_2O line at 1330 cm^{-1}. (L = 64 cm)

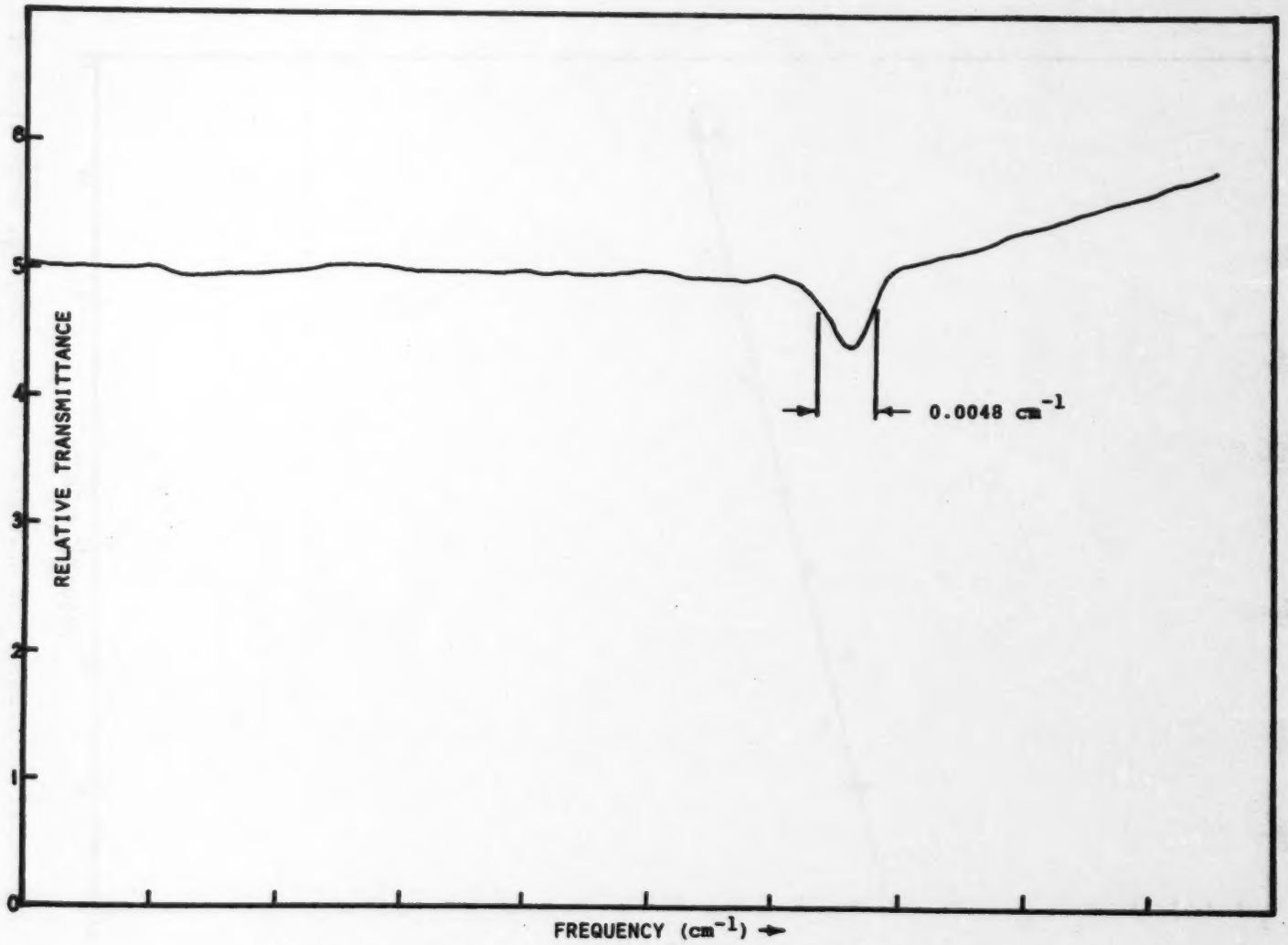

Figure 30. H_2O line at 1330 cm^{-1} above a 150°C H_2SO_4 azeotrope
L=64 cm, T_{body}=170°C

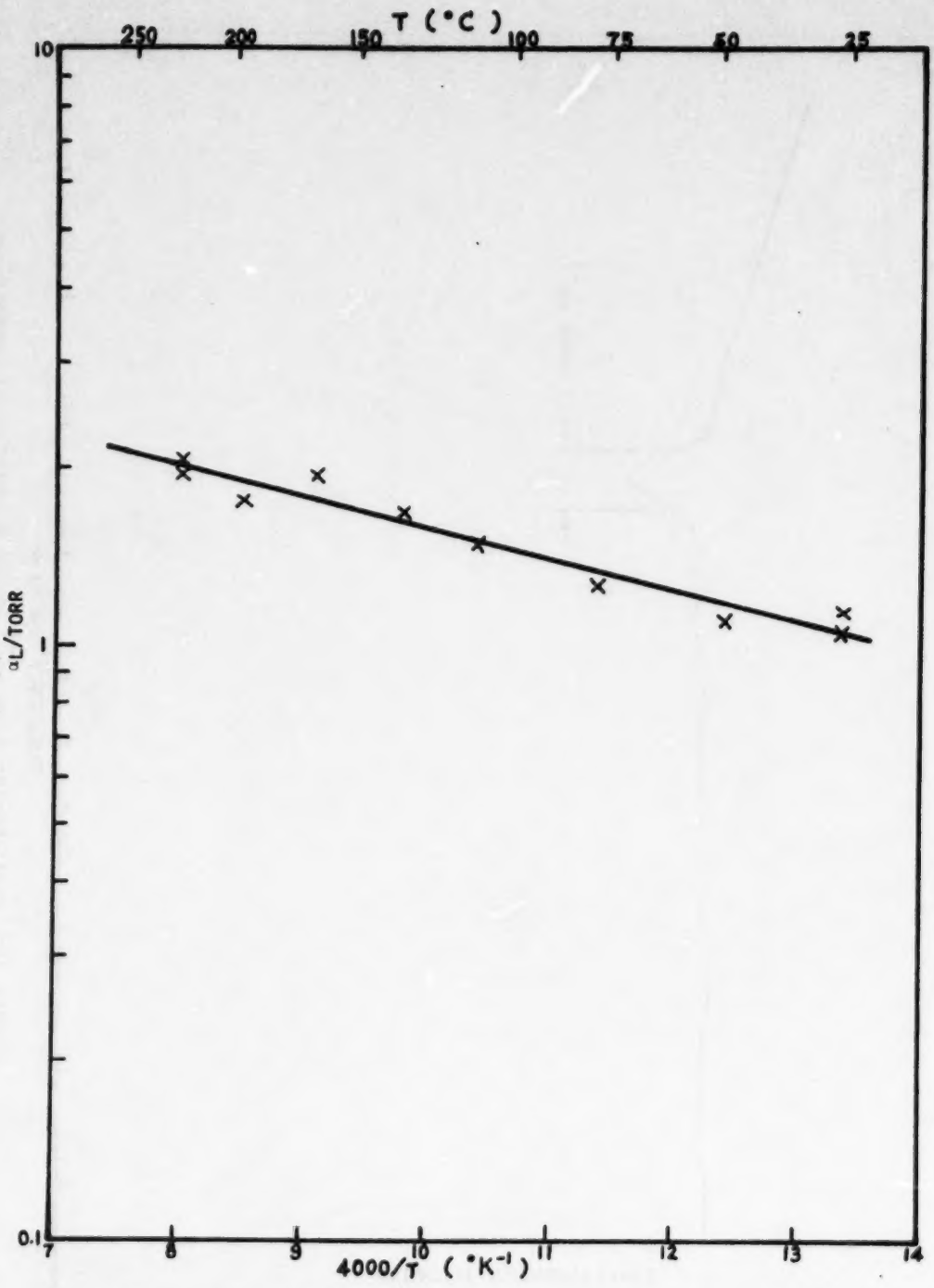

Figure 31. Absorbance per unit pressure (αL/Torr) vs. temperature of cell body for the SO_3 line near 1354 cm^{-1} (L=64 cm)

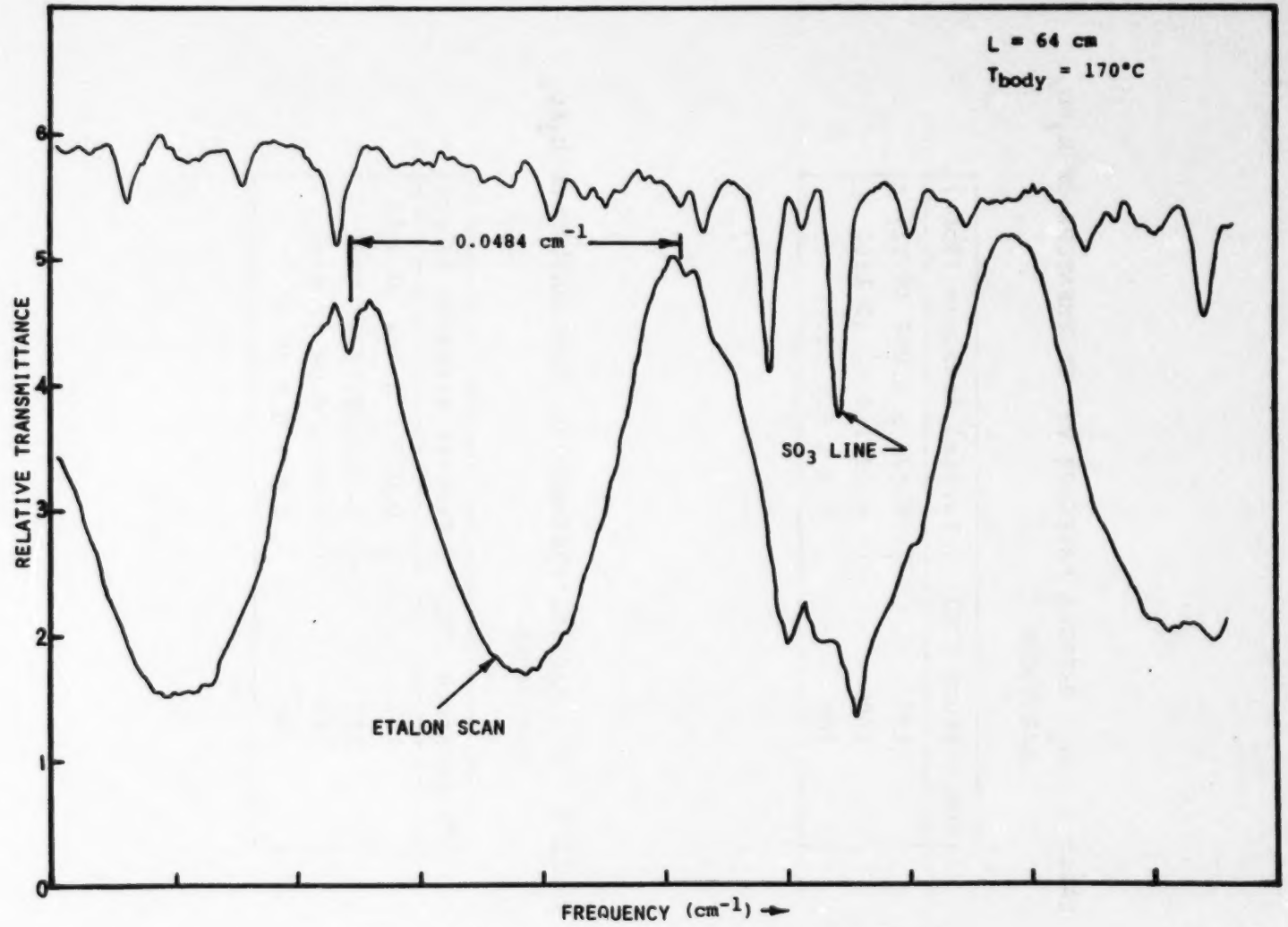

Figure 32. SO_3 absorption lines near 1354 cm^{-1}

TABLE 1. H_2O PARTIAL PRESSURE VS. TEMPERATURE OF H_2SO_4 AZEOTROPE

Temperature (°C)	Partial Pressure (Torr)
107	0.024 ± 0.002 (0.01)
150	0.23 ± 0.02 (0.145)
200	2.3 ± 0.2 (1.7)

TABLE 2. SO_3 PARTIAL PRESSURE VS. TEMPERATURE OF H_2SO_4 AZEOTROPE

Temperature (°C)	Partial Pressure (Torr)
107	0.022 ± 0.002 (0.005)
150	0.21 ± 0.02 (0.086)
180	0.90 ± 0.09 (0.43)
200	2.0 ± 0.2 (1.3)

Total Pressure Measurements--

Since it was not possible to isolate any single H_2SO_4 line for absorption strength measurements and since H_2SO_4 vapor does not exist by itself alone, the partial pressure of H_2SO_4 cannot be measured independently; therefore, it was necessary to measure the total vapor pressure and then determine indirectly the partial pressure of H_2SO_4 by subtracting the H_2O and SO_3 partial pressures from the total pressure. The apparatus used for measuring the total pressure consists of a pyrex "U" tube manometer connected to a glas bulb containing the azeotrope. Figure 33 is a sketch of the total pressure measuring apparatus. Azeotrope prepared by distillation was placed in the bulb (the "U" tube at this time had no azeotrope liquid). The space above the bulb and the entire "U" tube section were exhausted to high vacuum. This was done with the oil bath near room temperature. Valve A was then closed. The "U" tube was then filled to level as shown with liquid from the bulb by tilting the apparatus momentarily. The temperature of the bath and the section of the "U" tube covered by the heating tape was then brought up to the azeotrope temperature (100°C, 150°C or 200°C) with the glass tubing being ~15°C hotter than the bath. As the total pressure above H_2SO_4 solution increased, a sufficient amount of dry nitrogen was let into the right hand side of the "U" tube to keep the liquid levels on both sides equal. When this occurred, the total vapor pressure would be exactly equal to the pressure gauge reading.

As a check, the apparatus was used to measure the water vapor pressure at about 40 Torr. The result indicated that the measurement was accurate to less than one Torr. Since the H_2SO_4 azeotrope has a specific gravity of about 1.83 and the liquid level can be read to about 1/2 mm, the reading error is about 0.07 Torr. Table 3 is a summary of the total vapor pressure measurements. The overall error includes the liquid level reading error, pressure gauge inaccuracy, leveling of the "U" tube, an estimated error due to possible condensation of the vapor above the "U" tube liquid and oil bath temperature uncertainty.

Partial Pressure of H_2SO_4--

Table 4 lists the partial pressure of H_2SO_4 based on the total pressure and partial pressure measurements discussed in the preceding paragraphs. As mentioned in the beginning of experimental methods for partial pressure determination, the partial pressure of H_2SO_4 was equal to the difference between the total pressure and the sum of the SO_3 and H_2O pressures. It can be seen that the partial pressure is considerably lower than those from Luchinskii based on the 98.3% azeotrope. Therefore, as a result, the absorption coeffijient of H_2SO_4 vapor is correspondingly higher. For example, previously we obtained an atmospheric H_2SO_4 absorption coefficient of about 4.9×10^{-4} $ppm^{-1}\text{-}m^{-1}$ based on Luchinskii's pressure data. Based on our new pressure data, the coefficient should now be 6.4×10^{-4} $ppm^{-1}\text{-}m^{-1}$.

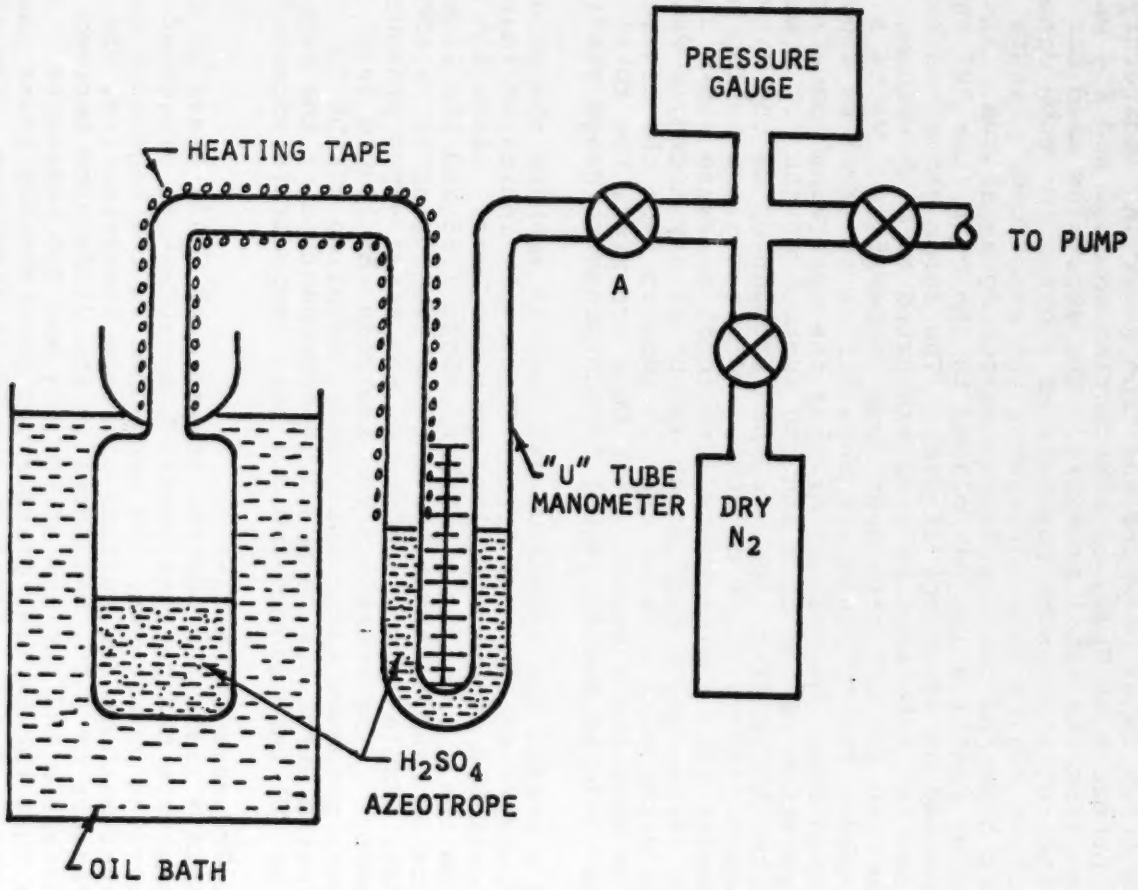

Figure 33. Total pressure measurement apparatus

TABLE 3. TOTAL PRESSURE VS. TEMPERATURE OF H_2SO_4 AZEOTROPE

Temperature (°C)	Total Pressure (Torr)
107	0.08 ± 0.02 (0.055)
150	0.75 ± 0.08 (0.68)
200	7.8 ± 0.8 (7.46)
232	23 ± 2 (26.2)

TABLE 4. H_2SO_4 PARTIAL PRESSURE VS. TEMPERATURE OF H_2SO_4 AZEOTROPE

Temperature (°C)	Partial Pressure (Torr)
107	0.034 ± 0.02 (0.04)
150	0.32 ± 0.08 (0.45)
200	3.5 ± 0.8 (4.4)

Based on our experimental results, we computed the azeotrope composition and dissociation constant K_p. Table 5 is a list of the azeotropic composition vs. temperature and Fig. 34 is the K_p constant vs. temperature. The dissociation constant of K_p was calculated from the partial pressures given in Tables 1, 2 and 4 for three azeotrope reservoir temperatures, namely 107°C, 150°C and 200°C. Since the cell body temperature was 20°C higher in each case, the calculated K_p was assigned to the corresponding cell body temperature at 127°C, 170°C or 220°C. Figure 34 shows that the dissociation constant agrees well with the extrapolated value from Gmitro's plot. The spectroscopic technique has greatly extended the measurable range of the dissociation constant to lower temperature. Although the partial vapor pressure of H_2O above H_2SO_4 azeotrope near room temperature is very low, the present spectroscopic method is capable of determining the dissociation constant of H_2SO_4 near room temperature.

Finally, Fig. 35 is the plot of vapor pressure vs. temperature for H_2O, SO_3 and H_2SO_4. For completeness, the atmospheric azeotrope data previously measured are also included (8).

As mentioned in the preceding paragraphs, our measured H_2SO_4 partial pressures are about 30% lower than those from Luchinskii and our measured H_2O and SO_3 partial pressures are considerably higher than those from Luchinskii. The effect of further dissociation of H_2SO_4 on going from the reservoir to the hotter cell body (20°C higher in temperature than the reservoir) could account for the discrepancy.

The following paragraphs show that the measured partial pressures are in good agreement with the calculated values taking dissociation into consideration.

In the atmospheric scan, in which the reservoir temperature was 200°C and the cell body was at 230°C, a value of absorbance equal to 2.028 ($\alpha L = \ell n\ I_o/I = \ell n\ 15.2/2.0$) was obtained (see Fig. 17). Since the cell length was 64 cm and the measured H_2SO_4 partial pressure at 200°C reservoir temperature (Table 4) was 3.5 Torr, the absorption coefficient for the 880 cm^{-1} band was calculated to be

$$\alpha = \frac{2.028}{L}\,\frac{760}{3.5} = \frac{2.028}{64}\,\frac{(760)}{3.5} = 6.88\ cm^{-1}/atm$$

which was plotted in Fig. 21.

We will now show that the observed value of H_2SO_4 partial pressure, 3.5 Torr (which we determined using the spectroscopic techniques to measure partial pressures) was the result of further dissociation of H_2SO_4 vapor from the 200°C reservoir on going to the 220°C cell body. The other measured pressures were P_{SO_3} = 2.1 Torr, P_{H_2O} = 2.3 Torr and P_{total} = 7.8 Torr. From

TABLE 5. AZEOTROPIC COMPOSITION VS. TEMPERATURE OF H_2SO_4 AZEOTROPE

Temperature °C	Azeotropic Composition (% H_2SO_4)
107	99.35
150	99.31
200	99.01
326	98.48

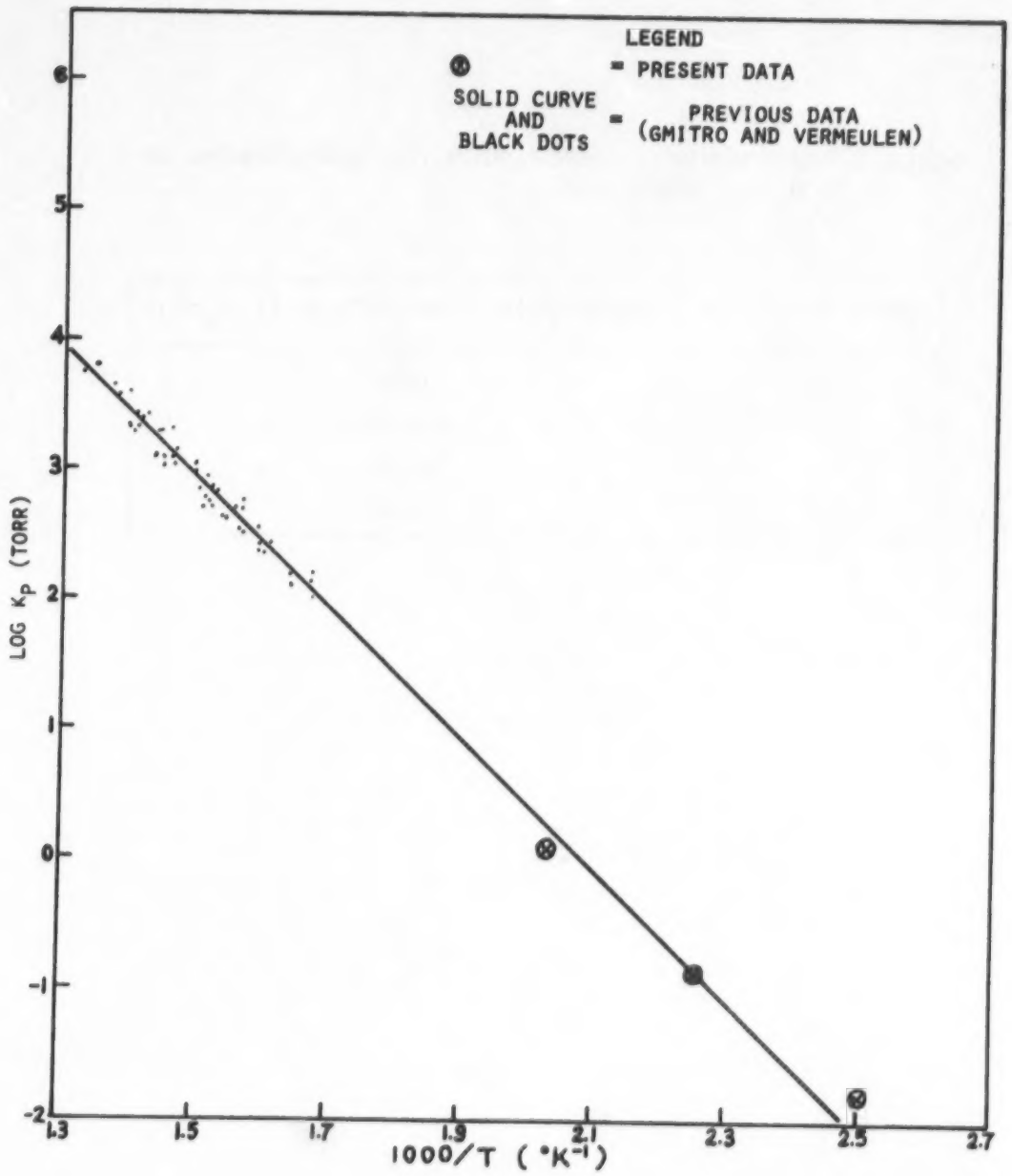

Figure 34. Dissociation constant K_p of H_2SO_4 gas vs. temperature

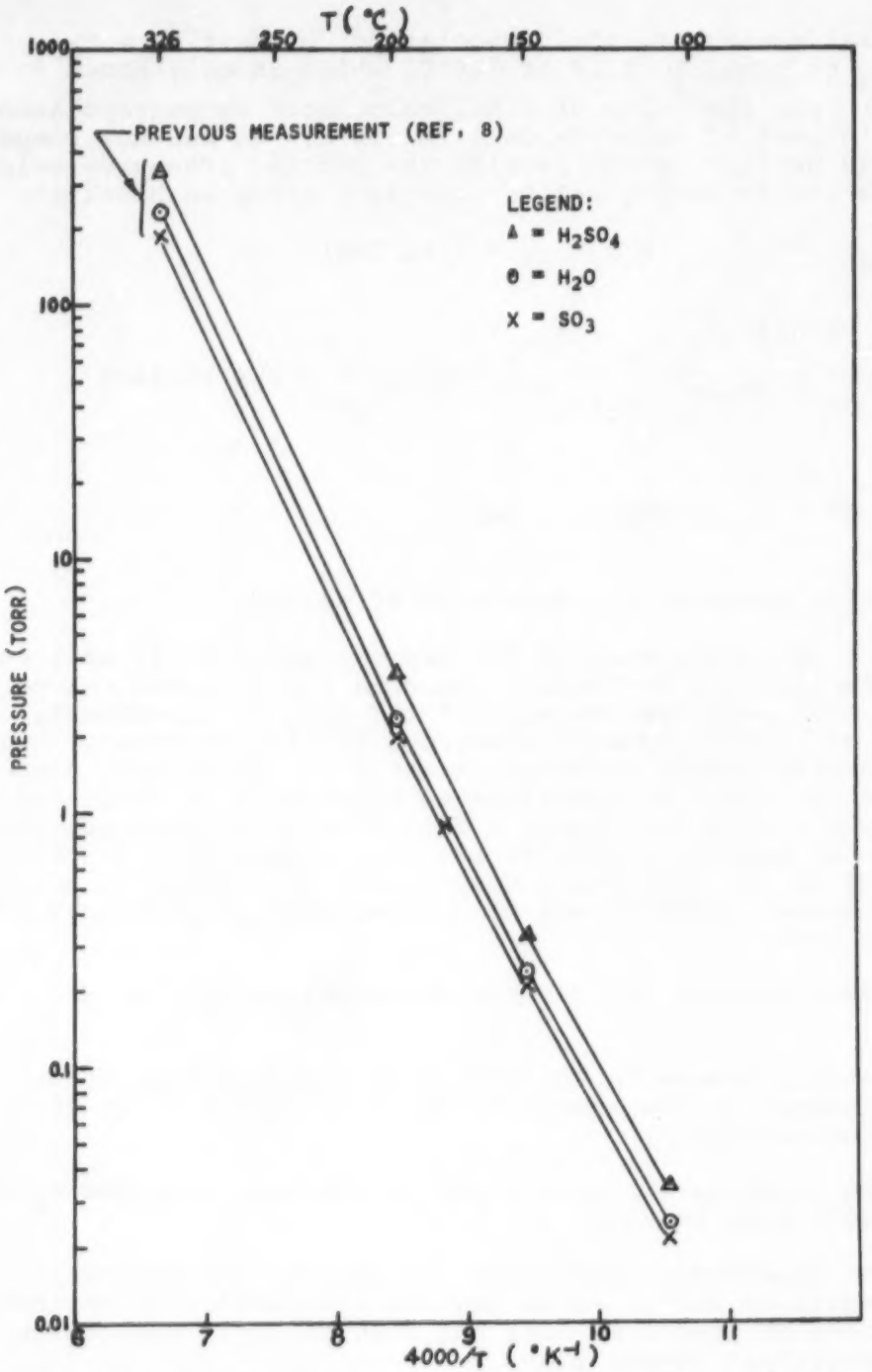

Figure 35. Partial pressure of H_2SO_4, H_2O and SO_3 above azeotropic H_2SO_4 solution vs. temperature

these partial pressures, the dissociation constant $K_p = P_{SO_3} \cdot P_{H_2O}/P_{H_2SO_4}$ is equal to 1.38 at 220°C, which is only about 11% smaller than the value of 1.541 calculated by extrapolating Luchinskii's partial pressure data to 220°C. We can now compare our observed partial pressures with the partial pressures calculated using the following set of equations (from Luchinskii).

$$P_{H_2O} + P_{SO_3} + P_{H_2SO_4} = P_{total} = 7.65 \text{ Torr} \quad (1)$$

$$\frac{98.082\ (P_{H_2SO_4} + P_{SO_3})}{80.066\ (P_{SO_3}) + 98.082\ P_{H_2SO_4} + 18.016\ P_{H_2O}} = W = 99.144\% \quad (2)$$

$$\frac{P_{H_2O} \cdot P_{SO_3}}{P_{H_2SO_4}} = K_p\ (220°C) = 1.541 \quad (3)$$

where W is the azeotropic composition by weight.

Table 6 shows the results for two values of W, 99.144% and 98.402%. The last row in Table 6 contains the observed values. Two values of W were used because of the lack of experimental data for W vs. total pressure azeotrope in the low pressure range. Based on Kunzler's data on total pressure vs. azeotropic composition (see Fig. 36), an extrapolated value of W is estimated to be about 99.0 ± 0.2% for P_{total} = 7.65 Torr. It turns out that the calculated partial pressures are very insensitive to this small change in the azeotropic composition (see Table 6). The agreement between observed and calculated partial pressures are indeed very good.

The justification for the use of Equations (1),(2) and (3) are

1. total pressure in the cell body is controlled by the pressure at the reservoir which is 7.65 Torr at 200°C (Luchinskii)

2. the dissociation took place in the cell body and K_p at 220°C must be used

3. the azeotropic composition is that of the reservoir liquid at 200°C, since heating the gaseous constituents above an azeotrope does not significantly change its azeotropic composition.

It appears from the above discussion on the partial pressure measurements and independently calculated results that the H_2SO_4 partial pressure was valid as measured, and Equations (1), (2)

TABLE 6. CALCULATED PARTIAL PRESSURES INCLUDING THE EFFECTS OF DISSOCIATION

W(%)	Pressures(Torr)				Method
	H_2O	SO_3	H_2SO_4	Total	
99.144	2.349	2.1	3.201	7.65	calc.
98.402	2.459	2.0	3.191	7.65	calc.
99.01	2.3	2.0	3.5	7.8	observed

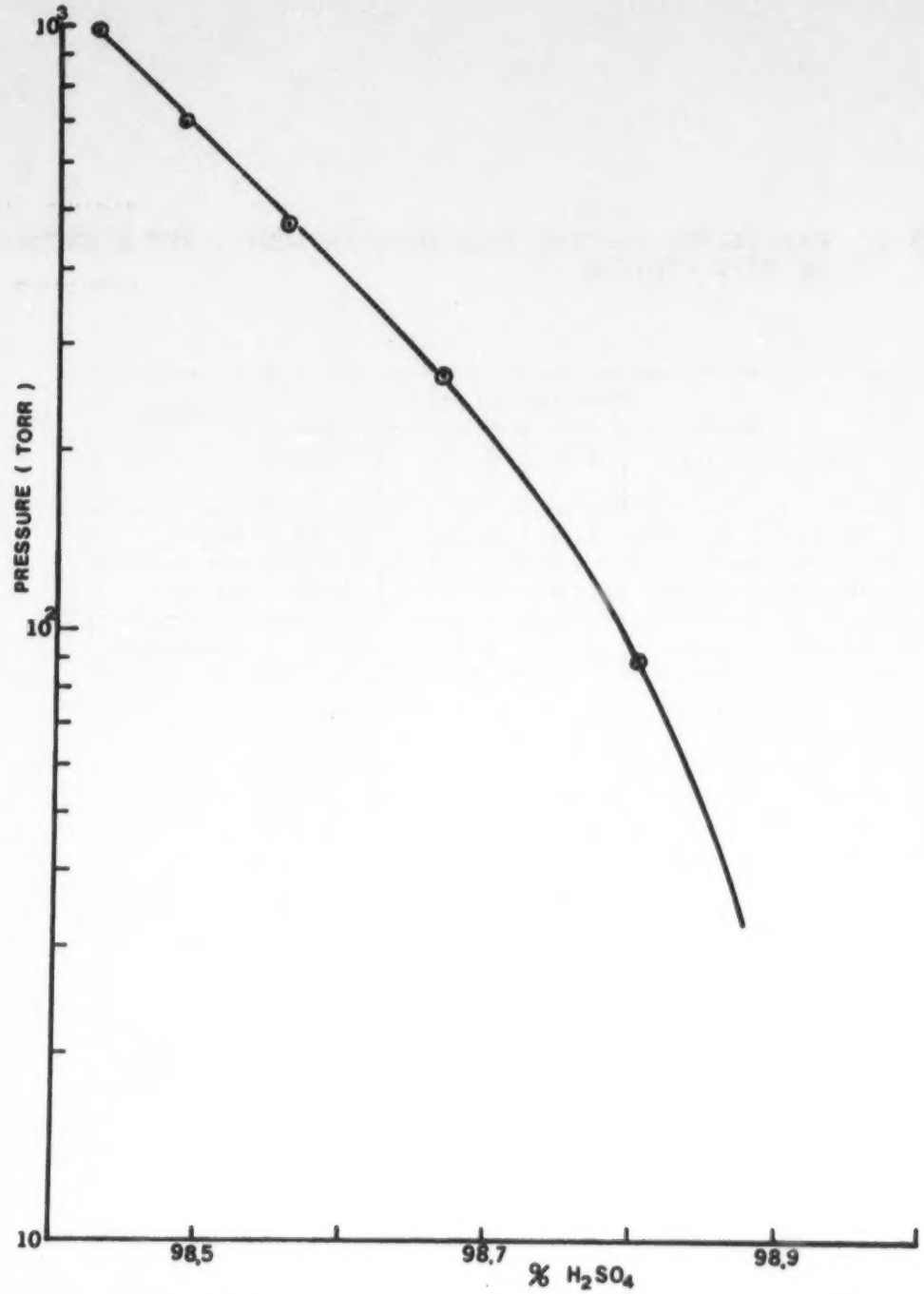

Figure 36. Total vapor pressure above H_2SO_4 solution vs. azeotropic composition

and (3) can be used with confidence to determine the partial pressure of H_2SO_4.

A careful comparison of the experimental conditions between the atmospheric scan and the low pressure scan (partial pressure measurements) shows that one cannot use these three equations to calculate the H_2SO_4 pressure for the atmospheric scan. The reason is that the gas in the atmospheric scan was flowing into the cell body from the reservoir and the total pressure of the constituent gases (H_2O, SO_3 and H_2SO_4) was not constrained to the reservoir pressure. If the cell body were at the same temperature as the reservoir (200°C), the total pressure of the constituent gases would be 7.65 Torr. As much as the cell body was maintained at 230°C more H_2SO_4 vapor would be dissociated according to the following relationship

$$K_p(230°C) = 1.99 = \frac{(P_{H_2O} + \Delta P)(P_{SO_3} + \Delta P)}{(P_{H_2SO_4} - \Delta P)} \qquad (4)$$

where ΔP is the change in pressure due to dissociation. The value of 1.99 was again based on extrapolated partial pressure values from Luchinskii's data. P_{H_2O} = 1.81 Torr, P_{SO_3} = 1.3 Torr and $P_{H_2SO_4}$ = 4.54 Torr to be used in Equation (4) as the pressures at the reservoir. Solving for ΔP, we obtained ΔP = 1.081 Torr. The final pressures in the cell body are then P_{H_2O} = 2.891 Torr, P_{SO_3} = 2.38 Torr, $P_{H_2SO_4}$ = 3.459 Torr and P_{total} = 8.731 Torr. The buffer gas nitrogen at 1 atm is assumed to have no influence at the dissociation coefficient K_p. Based on this value of H_2SO_4 partial pressure, the peak absorption coefficient at atmospheric pressure is 6.87 cm^{-1}/atm in the 880 cm^{-1} and about 6.46 cm^{-1}/atm in the 1220 cm^{-1} region. These values are valid for a cell wall temperature of 230°C. The absorption coefficient should remain relatively unchanged in the 200-250°C range if it is assumed that the individual H_2SO_4 lines making up the absorption profiles are relatively independent of temperature.

By considering the effects of dissociation we find that our results for the partial pressures are in better agreement with previous determinations and that our absorption coefficient remains essentially unchanged from that determined from the results of transmission measurement and partial pressure measurement.